#3 ER894787055US

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 3 : D21C 11/04, 11/12

A1

(11) International Publication Number: WO 84/ 04552

(43) International Publication Date: 22 November 1984 (22.11.84)

(21) International Application Number: PCT/US84/00739

(22) International Filing Date: 16 May 1984 (16.05.84)

(31) Priority Application Number: 495,847

(32) Priority Date: 18 May 1983 (18.05.83)

(33) Priority Country: US

(71) Applicant: WEYERHAEUSER COMPANY [US/US]; Tacoma, WA 98477 (US).

(72) Inventors: SPEAKS, Jerry, Robert ; 5547 Beverly Avenue North East, Tacoma, WA 98422 (US). McCALL, Thomas, Franklin ; Route 10, Box 366, Columbus, MS 39701 (US). WARRICK, Ronald, Paul ; 25 Pike Street North East, Auburn, WA 98002 (US).

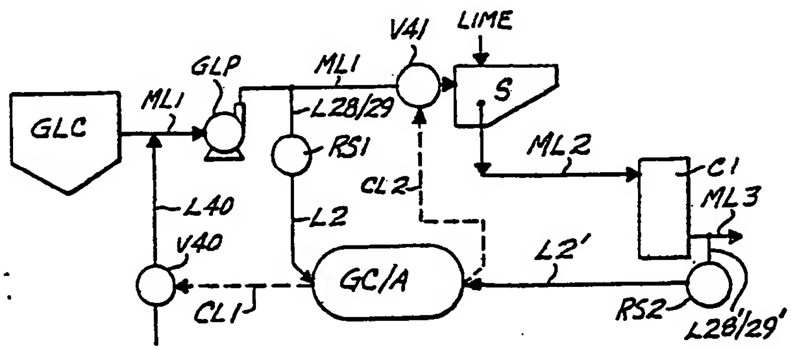
(74) Agents: CRAWFORD, John, M. et al.; Patent Department CH 2J29, Weyerhaeuser Company, Tacoma, WA 98477 (US).

(81) Designated States: FI, FR (European patent), JP, NO, SE (European patent).

Published
With international search report.

(54) Title: METHOD AND APPARATUS FOR ANALYZING AND CONTROLLING CARBONATE AND SULFIDE IN GREEN LIQUOR SLAKING AND CAUSTICIZING

(57) Abstract



A process and apparatus for measuring carbonate and sulfide concentrations in white and green pulping liquor and in the slaker/causticizing (S, C_1) cells and controlling the causticizing reaction and other stages using this information. Specifically the causticizing control logic is based on determining the concentration of sodium carbonate and sodium sulfide (GC/A) in the green liquor, in the white liquor-mud slurry at the slaker or first causticizer (ML3) and in the white liquor being sent to the digester house and using this information to control the entire process. Th e concentration and flow rate of the green liquor may be measured and controlled quite easily. The proposed strategy will control the green liquor flow rate (V41) to the slaker to maintain the desired Na_2CO_3 concentration in the slaker/causticizer liquor despite variations which occur in the lime. The green liquor concentration is also controlled in a control loop. Weak wash liquor (L40) is added to the green liquor to maintain the concentration of the Na_2CO_3 in the green liquor. The slaking/causticizing process is controlled by adjusting the flow rate and concentration of the green liquor. This strategy will control the process based on direct measurements of the critical component in the system, sodium carbonate. The green liquor flow rate will be automatically adjusted by a control loop to maintain the desired Na_2CO_3 concentration in the white liquor. The last measurement is to determine the concentrations of sodium hydroxide, sodium carbonate, and sodium sulfide in the white liquor which is sent to the digester house to be used in the cooking process. It is important to measure the sodium hydroxide and sodium sulfide concentrations in the white liquor (RS3, GC/A) so that the amount of liquor to be charged in the digester(s) may be correctly determined. Changes in sodium sulfide concentration (generated at the recovery boiler) can affect white liquor (AA/EA) concentration.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	KR	Republic of Corea
AU	Australia	LI	Liechtenstein
BE	Belgium	LK	Sri Lanka
BG	Bulgaria	LU	Luxembourg
BR	Brazil	MC	Monaco
CF	Central African Republic	MG	Madagascar
CG	Congo	MR	Mauritania
CH	Switzerland	MW	Malawi
CM	Cameroon	NL	Netherlands
DE	Germany, Federal Republic of	NO	Norway
DK	Denmark	RO	Romania
FI	Finland	SD	Sudan
FR	France	SE	Sweden
GA	Gabon	SN	Senegal
GB	United Kingdom	SU	Soviet Union
HU	Hungary	TD	Chad
JP	Japan	TG	Togo
KP	Democratic People's Republic of Korea	US	United States of America

METHOD AND APPARATUS FOR ANALYZING AND CONTROLLING CARBONATE AND SULFIDE IN GREEN LIQUOR SLAKING AND CAUSTICIZING

BACKGROUND OF THE INVENTION

Field of the Invention

Analyzing green liquor, slaker and causticizing cells, and white liquor chemicals and controlling pulp mill operations from the analysis.

Other Art

A good diagram of the causticizing process may be found in Pulp and Paper Manufacture, 2nd Ed., Volume I, The Pulping of Wood, 1969, prepared under the direction of the Joint Textbook Committee of the Paper Industry, R. G. MacDonald, editor, and J. N. Franklin, technical editor, the McGraw Hill Book Company, New York, publisher. The diagram is Figure 9-72 on page 535.

The process actually starts with the recovery furnace. The black liquor consisting of organic and inorganic chemicals and water is charged to the furnace where the water is evaporated, the organic components are burned and inorganic components are recovered in the form of a molten smelt. The molten smelt containing mostly sodium carbonate and sodium sulfide is continuously decanted from the furnace bed and dissolved in water (weak wash) at the dissolving tank or tanks to form green liquor. A typical green liquor composition is about 60-65% sodium carbonate and 25-28% sodium sulfide by weight (% of solids) expressed as Na_2O. A typical solids content of green liquor is around 18% of total liquor weight. The green liquor is pumped from the dissolving tank or tanks to a green liquor clarifier where the dregs settle out. The dregs are impurities, i.e., undissolved solids from the furnace. These are mainly carbon, calcium, magnesium and iron compounds.

Following clarification, the green liquor is mixed with reburned lime from the kiln in the slaker. Usually the amount of lime is adjusted to maintain a specified white liquor concentration. Makeup lime in the form of fresh lime (or limestone burned in the kiln) is added to the reburned lime to replace lime losses in the system. Grits (large, unreacted lime particles) are removed from the slaked lime slurry in the classifier section of the slaker. In the slaker the lime or calcium oxide reacts with the water in the green

liquor to form calcium hydroxide and this in turn reacts with the sodium carbonate in the green liquor to form sodium hydroxide and calcium carbonate, which then flows to the causticizing cells. Causticizing cells are used to allow enough time for the causticizing reaction that starts in the slaker to approach completion. From the causticizers, the slurry is pumped to the white liquor clarifier (or a pressure filter) to separate the white liquor from the lime mud, calcium carbonate. The clarified white liquor is pumped to storage and then to the digester house to pulp wood chips. The mud or calcium carbonate in the bottom of the clarifier is pumped to a mud washer where it is washed with water from the mud filter and the dregs washer. The overflow water from the mud washer is called weak wash and this is used at the dissolving tank or tanks to dissolve the smelt to form raw green liquor.

In the usual process then, weak wash is used at the dissolving tank or tanks to dissolve the molten sodium salts exiting from the recovery boiler. The resulting raw green liquor is then clarified to remove the dregs and then pumped to the slaker. Lime feed to the slaker is generally based on the total flow of green liquor and the slaker temperature, the slaker temperature specification being such as to maintain a specified white liquor strength and safe operating conditions.

The causticizing reaction is usually controlled by chemical analysis (titration) of the white liquor taken from a causticizing cell or from the white liquor clarifier overflow. Lime feed, green liquor density at the dissolving tank or tanks or a combination of the two is usually changed to maintain a white liquor strength within a mill's specification. The specification is generally expressed as the sodium hydroxide and sodium sulfide concentration in the white liquor, i.e., AA (active alkali) or EA (effective alkali). These expressions are defined and discussed on pp. 358-363 of MacDonald and Franklin, supra.

White liquor AA or EA concentration does vary considerably because of changes in lime availability (CaO content), reactivity (rate of hydration), mass flow rate of lime to the slaker or combinations of these. Sodium carbonate concentration changes in the green liquor feed will also affect the resulting white liquor strength. The presence of this number of uncontrolled variables makes it very difficult to control the slaking/causticizing reaction.

Present practice uses a total titratable alkali (TTA) measurement to control liquor strength and causticizing efficiency. TTA is a measurement of sodium hydroxide, sodium carbonate, and sodium sulfide, and is, therefore, only an indirect, approximate determination of the Na_2CO_3 concentration in the liquor.

Another variable that makes slaker control difficult is the colorimetric titration (ABC test) used to analyze the liquor. The ABC test is found in TAPPI test T624 OS-68 (Parts 9, 10 and 11). It may be modified to fit specific mill conditions. Titration end points are not identified by a crisp color change. Rather, there is a gradual change in color, for example, from orange to red or from green to blue depending on which indicator is used. This "diffuse" end point determination results in much uncertainty in the liquor concentrations which are the only variables which are measured regularly.

There have been attempts to solve these problems. Hultman, et al, U.S. Patents 4,236,960 and 4,311,666 describe a different type of process for controlling the degree of causticizion. Sutinan and Haapoja, "Causticizing Plant and Lime Kiln Computer Control" describes a Nokia Autolime system.

TAPPI test T624 OS-68 describes tests for the analysis of soda and sulfite white and green liquors. Test 12 describes the sodium carbonate (evaluation method) test.

SUMMARY OF THE INVENTION

A process and apparatus for measuring carbonate and sulfide concentrations in white and green pulping liquor and in the slaker and causticizing cells and controlling the causticizing reaction and other stages using this information.

The proposed process control logic reduces or eliminates most of the above-mentioned process control problems. It is based on the idea that a kraft mill slaker is really a carbonate reactor, i.e., carbonate ions in the green liquor are crystallized from solution with hydrated lime, and sodium hydroxide is generated in the process. Specifically the causticizing control logic is based on determining the concentration of sodium carbonate and sodium sulfide in the green liquor, in the white liquor-mud slurry at the slaker or first causticizer and in the white liquor being sent to the digester house and using this information to control the entire process. This logic is much different than present practice.

The reason for measuring the concentration of sodium sulfide in the green liquor is not to control the slaking/causticizing process, but to indicate inefficiencies in the process and to take steps to control them. An increase in sulfide concentration will tend to decrease the efficiency of the causticizing reaction. Knowledge of the concentration of sodium sulfide entering the slaker will indicate to the operator or process computer the optimum causticizing efficiency that can be expected from his recausticizing plant. The changes in sulfide concentration will also indicate changes in recovery boiler sodium sulfide reduction efficiency and will allow steps to be taken to better control boiler sodium sulfide reduction efficiency.

It is desired that as much of the sodium carbonate in the green liquor as possible be converted to sodium hydroxide in the slaker and causticizers. It is impossible to completely convert all the sodium carbonate to sodium hydroxide - some sodium carbonate will remain in the white liquor. The ultimate limit as to how much sodium carbonate may be converted to sodium hydroxide is governed by the equilibrium causticizing efficiency. A discussion of the factors governing the equilibrium causticizing efficiency may be found on pp. 532-534 of MacDonald and Franklin, supra.

It is desirable to maintain the final white liquor at a composition very close to that determined by the equilibrium causticizing efficiency. If this is performed correctly, the benefits will be high efficiency of operation due to efficient conversion of sodium carbonate to sodium hydroxide, and low sodium carbonate "deadload" in the white liquor, which has many benefits throughout digestion, evaporation and recovery. In order to achieve this, it is necessary to closely balance the amounts of lime and green liquor being added to the slaker. An excess of green liquor to lime will result in low conversion efficiency of sodium carbonate to sodium hydroxide. An excess of lime to green liquor will impair the settling and filtering characteristics of the calcium carbonate "mud," which must be removed from the white liquor before it can be used in the digesters.

Variations in the Na_2CO_3 concentration in the liquor at the slaker or causticizer are the result of variations in the concentration and flow rate of lime and green liquor. Lime quality and quantity can be variable and difficult to control - changes in mass flow rate, availability (% CaO) and lime reactivity (how fast hydration occurs) affect the Na_2CO_3

concentration in the slaker/causticizer liquor, but are extremely difficult to measure and control. However, the concentration and flow rate of the green liquor may be measured and controlled quite easily. The proposed strategy will control the green liquor flow rate to the slaker to maintain the desired Na_2CO_3 concentration in the slaker/causticizer liquor despite variations which occur in the lime. The green liquor concentration is also controlled in a control loop. The advantages of this strategy are as follows:

1. A constant, desired concentration of Na_2CO_3 is controlled early in the slaking/causticizing reaction, ensuring safe, efficient operation.

2. The slaking/causticizing process is controlled by adjusting the flow rate and concentration of the green liquor, which is technically quite easy to accomplish. Controlling the concentration, activity, and flow rate of the lime is technically difficult and therefore is allowed to vary within normal limits and the green liquor flow rate is adjusted in response to these variations. This strategy provides much more precise control than do strategies which attempt to adjust lime flow rate in response to changes in liquor flow rate and concentration.

3. This strategy will control the process based on direct measurements of the critical component in the system, sodium carbonate. This provides much more precise control than do strategies based on TTA liquor conductivity, liquor density or other indirect, approximate indications of Na_2CO_3 in process liquors.

The overall liquor room production rate (amount of white liquor generated per minute) will be controlled by the flow rate of lime to the slaker. As the production rate needs to be increased or decreased in order to maintain an overall mill liquor balance, the flow rate of lime added to the slaker is correspondingly increased or decreased. The green liquor flow rate will be automatically adjusted by a control loop to maintain the desired Na_2CO_3 concentration in the white liquor. Both chemical inventory (lime and liquor storage levels) and mill production rates can be maintained by this strategy. Chemical inventory and/or production rate may be controlled either manually or automatically.

The last measurement is to determine the concentrations of sodium hydroxide, sodium carbonate, and sodium sulfide in the white liquor which is sent to the digester house to be used in the cooking process. It is important to measure the sodium hydroxide and sodium sulfide

concentrations in the white liquor so that the amount of liquor to be charged in the digester(s) may be correctly determined. Changes in sodium sulfide concentration (generated at the recovery boiler) can affect white liquor AA/EA concentration.

The apparatus takes a sample from an appropriate line - green liquor, slaker/causticizer liquor, or white liquor to the digester - filters the sample if necessary, takes a measured quantity, reacts that measured quantity with an acid to generate hydrogen sulfide and carbon dioxide and measures the quantities of these gases in a gas chromatograph. The apparatus has four main circuits: the filter circuit, the sampling circuit, the reactor circuit and the gas chromatograph circuit. A mud separation circuit is also utilized if the apparatus is to analyze liquor from the slaker or causticizing cells. A number of operations or modes are performed in each of these circuits during a test cycle. These modes are sequenced differently depending upon the different operation of the mill.

The unit must operate consistently over a long period of time and must give reproducible results. For example, the liquor is corrosive and can also plug lines. The inventors have devised an apparatus which eliminates corrosion and reduces line plugging to a minimum. This required a great deal of lab and mill testing and redesign to accomplish. During the testing, it was found that the liquor being analyzed, the degree of completion of the reaction and the temperature of the reactive gases would cause changes in the results which would lead to an inability to control the process. Again, a great deal of time and laboratory and mill testing was required before the problem was recognized, the sources of the problem discovered and corrective measures taken. The present apparatus and control logic is the result of several man-years of work extending over a several-year period and the present application represents the inventor's understanding as of the date of the application of the problem and the solution. The work is continuing.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram of the principal components of the test unit.

Figure 2 is a diagram of the filter circuit for the apparatus.

Figure 3 is a diagram of a three-filter circuit unit for the apparatus when operating in a three-component configuration.

Figure 4 is a diagram of the mud separation circuit.

Figure 5 is a cross-sectional view of the reactor for the apparatus.

Figure 6 is a top plan view of the reactor for the apparatus.

Figure 7 is an interior side plan view partially in cross section showing the magnetic spin bar driver and the spin bar in the reactor chamber.

Figure 8 is a cross-sectional view along line 8-8 of Figure 7.

Figure 9 is a plot of a gas chromatograph voltage output over the course of gas analysis resulting from a typical green liquor sample.

Figure 10 is a schematic diagram of a data collection circuit.

Figure 11 is a diagram of a single loop apparatus in a pulp mill.

Figure 12 is a diagram of a double loop apparatus in a pulp mill.

Figure 13 is a diagram of a triple loop apparatus in a pulp mill.

Figure 14 is a diagram of a cascaded control.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The apparatus has four main circuits: the filter circuit, the sampling circuit, the reactor circuit and the gas chromatograph circuit. A mud separation circuit is also used if the apparatus is to be utilized to analyze liquor from the slaker or causticizing cells. Each of these circuits has a number of operations or modes which are performed during one test cycle. These modes are sequenced differently depending upon the particular operation of a mill. The parts and modes will be described for each of the circuits. A possible sequence will then be described.

It should be noted that most of the operable valves throughout the unit are two-position valves. This is for ease and simplicity of operation. Three-position valves or multiple port valves are used in several specific applications. Where so used, the use of these valves is noted.

Filter Circuit

The purpose of the filter circuit is to remove particulate material from the liquor to prevent both the plugging of the test equipment and the chemical side reactions that would mask the true composition of the liquor.

The following description is directed to the filter circuit of Figures 2 and 3. Each of the filter circuits in the three circuit array shown in Figure 3 would have the same parts and operating sequence, so the same reference numerals will be used for the individual elements in these circuits.

The circuit has the following components:

Major components

F - Filter.

FS - Filter shock dome.

Lines

ML - Mill liquor line in the causticizing system between the green liquor clarifier and the slaker, between the slaker and first causticizer, between the first and second causticizers or between the clear white liquor storage tank and the digester, depending on the liquor being sampled.

L22 - Sampling line from the filter outlet line L30A to the sampling circuit.

L28 - Liquor return line from the filter circuit to the clarifier, slaker or causticizer depending on liquor being sampled.

L29 - Liquor supply line from the mill liquor line ML to the filter circuit.

L30 - Filter outlet line from the upper part of the filter F to the liquor return line L28.

L30A - Filter outlet line from the filter F to the sampling line L22.

L30B - Filter outlet line from the filter outlet line L30A to the filter backflush line L31.

L30C - Filter outlet line from the filter outlet line L30B to the liquor return line L28.

L31 - Filter backflush line from the valve V28 to the filter outlet line L30C.

L32 - Filter bypass line from the filter circuit inlet line L29 to the liquor return line L28.

L33 - Air inlet line to the top of the filter shock dome FS.

L33A - Air inlet line from the air supply to the water backflush line L37.

L33B - Air and water inlet line between the water backflush line L37 and the top of the filter shock dome FS.

L34 - Filter inlet and filter backflush outlet line between the valve V28 and the bottom of the filter F.

L35 - Inlet line from the filter circuit liquor supply line L29 to the valve V28.

L36 - Water supply line.

L37 - Water backflush line from the water supply line L36 to the inlet line L33B.

Valves

Operating valves (solenoid operated)

V21 - Valve in the filter outlet line L30A. Two positions: open; closed.

V22 - Valve in the sampling line L22. Two positions: open; closed.

V24 - Valve in the filter bypass line L32. Two positions: open; closed.

V26 - Valve in the air inlet line L33A. Two positions: open; closed.

V28 - Filter inlet-backflush three-way T valve at juncture of the filter backflush line L31, the filter inlet line L34 and the inlet line L35. Two positions: position one (backflush) (1B) - open to the filter backflush line L31 and the filter backflush outlet line L34, closed to the inlet line L35; position two (filter) (2F) - open to the filter inlet line L34 and the inlet line L35, closed to the filter backflush line L31.

V29 - Valve in the water backflush line L37. Two positions: open; closed.

Check valves

V18 - Check valve in the filter outlet line L30B to prevent flow through the line L30 into the filter F.

V23 - Check valve in the filter backflush line L31 to prevent flow through the line L31 into the filter F.

Pressure valve (open or partially open, manually operable)

V20 - Back pressure valve in the filter outlet line L30B to provide pressure in the filter F and to induce preferential flow into the sampling line L22 when the valve V22 is open.

Pressure relief valve (normally closed, automatically openable)

V27 - Pressure relief valve on the filter F.

Repair valves (normally open, manually operable)

V19 - Repair valve in the liquor return line L28.

V25 - Repair valve in the filter circuit liquor supply line L29.

The filter circuit has several operating modes.

Bypass mode (no liquor to filter) (Bypass)

The first mode is a liquor bypass mode in which the liquor is taken from the mill liquor line, through the bypass line and returned to the slaker or causticizer without passing through the filter.

Lines involved

ML - Mill liquor line.

L28 - Liquor return line from the filter circuit.

L29 - Liquor supply line from the mill liquor line ML to the filter circuit.

L32 - Filter bypass line from the filter circuit inlet line L29 to the filter circuit outlet line L28.

Valves involved

Operating valves/position

V21 - Valve in the filter outlet line L30A/closed.

V22 - Valve in the sampling line L22/closed.

V24 - Valve in the filter bypass line L32/open.

V26 - Valve in the air inlet line L33A/closed.

V28 - Filter inlet-backflush valve/position one (backflush) (1B) - open to the filter backflush line L31 and the filter backflush outlet line L34, closed to the inlet line L35.

V29 - Valve in the water backflush line L37/closed.

Check valves

V18 - Check valve in the filter outlet line L30B to prevent flow through the line L30 into the filter F.

V23 - Check valve in the filter backflush line L31 to prevent flow through the line L31 into the filter F.

Repair valves

V19 - Repair valve in the liquor return line L28.

V25 - Repair valve in the filter circuit liquor supply line L29.

Flow

ML through V25 through L29 through V24 through L32 through V19 through L28.

Time

The time will vary.

Liquor filtering mode (Filter)

The second mode is a liquor filtering mode in which the liquor is taken from the mill liquor line, filtered in the filter F and returned to the return line in order to establish steady state filtering of the liquor.

Major components involved

F - Filter

Lines involved

ML - Mill liquor line.

L28 - Return line from the filter circuit.

L29 - Liquor supply line from the mill liquor line ML to the filter circuit.

L30 - Filter outlet line from the upper part of the filter F to the return line L28.

L34 - Filter inlet line from the valve V28 to the bottom of the filter F.

L35 - Inlet line from the filter circuit liquor supply line L29 to the valve V28.

Valves involved

Operating valves/position

V21 - Valve in the filter outlet line L30A/open.

V22 - Valve in the sampling line L22/closed.

V24 - Valve in the filter bypass line L32/closed.

V26 - Valve in the air inlet line L33A/closed.

V28 - Filter inlet-backflush valve/position two (filter) (2F) - open to the filter inlet line L34 and the inlet line L35, closed to the filter backflush line L31.

V29 - Valve in the water backflush line L37/closed.

Check valves

V18 - Check valve in the filter outlet line L30B to prevent flow through the line L30 into the filter F.

V23 - Check valve in the filter backflush line L31 to prevent flow through the line L31 into the filter F.

Pressure valve

V20 - Back pressure valve in the filter outlet line L30B.

Repair valves

V19 - Repair valve in the filter circuit liquor return line L28.

V25 - Repair valve in the filter circuit liquor supply line L29.

Flow

ML through V25 through L29 through L35 through V28 through L34 through F through V21 through L30 through V20 through V18 through V19 through L28.

Note:

When first starting up the analyzer, a filter cycle is immediately performed to provide a liquor sample for the first reaction. For all subsequent reactions, the filter cycle is started at a time determined by an action somewhere else in the system. It can be started by a sequencer output which is energized when a new liquor sample is desired. This could be signaled by completion of filling the acid pump AP2 or opening the valve which applies pressure to the reactor R1.

Time

60 seconds - will vary depending on time required to fill lower part of filter with liquor and provide an adequate flow in L30 to provide a consistent liquor sample to the sample line L22.

Liquor sampling mode (sample)

~~The third mode is a liquor sampling~~ mode in which the liquor is taken from the mill liquor line, filtered and sent to the sampling circuit to provide the test sample. The parts, lines, valves and valve positions are the same in this mode as in the second mode, the filter mode, except for the following change.

Major components involved

F - Filter

Lines involved

L22 - Sampling line from the filter outlet line L30A to the sampling circuit.

Valves involved

Operating valves/position

V22 - Valve in the sampling line L22/open.

Pressure valves

V20 - Back pressure valve in the filter outlet line L30B provides back pressure to cause preferential diversion of the filtered liquor into the sampling line L22.

Flow

ML through V25 through L29 through L35 through V28 through L34 through F through V21 through L30A:

part through V22 through L22 to sampling circuit.

part through V20 through L30B through V18 through L30C through V19 through L28.

Time

60 seconds - will vary depending on time needed to completely flush and fill sample circuit with new liquor.

Stop sampling mode (Stop)

The fourth mode is a stop sampling mode which is a pause to allow the sample valve V22 in the sampling circuit to change position. The parts, lines, valves, valve positions and flows are the same as in the second mode - the filter mode.

Time

5 seconds or as needed to ensure closure of valve V22.

Liquor backflush mode

The fifth mode is a liquor backflush mode, in which the liquor is used to backflush or backwash particulate matter in the filter from the filter to the return line. It takes place in two stages.

Stage 1 (Backflush 1)

In stage 1 the filter outlet valve V21 is closed and liquor from the mill liquor line ML fills the filter to the middle of the filter shock dome FS.

Major components involved

F - Filter

FS - Filter shock dome.

Lines involved

ML - Mill liquor line.

L29 - Liquor supply line from the mill liquor line ML to the filter circuit.

L33 - Air inlet line to the top of the filter shock dome FS.

L34 - Filter inlet line from the valve V28 to the bottom of the filter F.

L35 - Inlet line from the filter circuit liquor supply line L29 to the valve V28.

Valves involved

Operating valves/position

V21 - Valve in the filter outlet line L30A/closed.

V22 - Valve in the sampling line L22/closed.

V24 - Valve in the filter bypass line L32/closed.

V26 - Valve in the air inlet line L33A/closed.

V28 - Filter inlet-backflush valve/position two (filter) (2F) - open to the filter inlet line L34 and the inlet line L35, closed to the filter backflush line L31.

V29 - Valve in the water backflush line L37/closed.

Repair valves

V25 - Repair valve in the filter circuit liquor supply line L29.

Flow

ML through V25 through L29 through L35 through V28 through L34 into F to middle of FS.

Time

10 seconds or as needed to provide sufficient liquor to backwash filter.

Stage 2 (Backflush 2)

In stage 2 air, admitted at the top of the filter shock dome FS, drives the liquor through the filter element of the filter F, out the inlet to the filter element, through the filter backflush outlet line L34, the backflush line L31, the filter outlet line L30C, and the filter circuit liquor return line L28.

Major components involved

F - Filter

Lines involved

L28 - Liquor return line from the filter circuit.

L30C- Filter outlet line from the filter backflush line L31 to the filter circuit liquor return line L28.

L31 - Filter backflush line from the valve V28 to the filter outlet line L30C.

L33 - Air inlet line to the top of the filter shock dome FS.

L34 - Filter backflush outlet line from the bottom of the filter F to the valve V28.

Valves involved

Operating valves/position

V21 - Valve in the filter outlet line L30A/closed.

V22 - Valve in the sampling line L22/closed.

V24 - Valve in the filter bypass line L32/open.

V26 - Valve in the air inlet line L33A/open.

V28 - Filter inlet-backflush valve/position one (backflush) (1B) - open to the filter backflush line L31 and the filter backflush outlet line L34, closed to the inlet line L35.

V29 - Valve in the water backflush line L37/closed.

Check valves

V18 - Check valve in the filter outlet line L30B to prevent flow through the line L30 into the filter F.

V23 - Check valve in the backflush line L31 to prevent flow through the line L31 into the filter F.

Repair valves

V19 - Repair valve in the filter circuit liquor return line L28.

Flow

Air

V26 through L33 into F.

Liquor

F through L34 through V28 through V23 through L31 through L30C through V19 through L28.

Time

15 seconds or as needed to adequately backflush filter.

Water backflush mode

The sixth mode is a water backflush mode in which water is introduced at the top of the filter shock dome FS and washes particulate

matter from the filter element, out the bottom of the filter through the filter backflush outlet line L34, the backflush line L31, the filter outlet line L30C, and the filter circuit liquor return line L28. The water backflush mode would normally occur in place of a first mode, a bypass mode, and would follow a fifth mode, the liquor backflush mode. It is used any time the filter is excessively dirty with particulate matter. The liquor supply would normally be turned off. The parts, lines, valves and valve positions are the same as in stage 2 of the fifth mode, stage 2 of the liquor backflush mode, with the following additions and changes.

<u>Lines involved</u>

L33A- Air line to the filter shock dome not used.

L33B- Inlet line from the water backflush line L37 to the top of the filter shock dome FS.

L36 - Water supply line.

L37 - Water backflush line from the water supply line L36 to the inlet line L33B.

<u>Valves involved</u>

<u>Operating valves/position</u>

V26 - Valve in the air inlet line L33A/closed.

V29 - Valve in the water backflush line L37/open.

<u>Flow</u>

<u>Water:</u>

L36 through V29 through L37 through L33B through F through L34 through V28 through V23 through L31 through L30C through V19 through L28.

<u>Time</u>

60 seconds or as needed to provide a complete washing of the filter element.

<u>Mud separation circuit - slaker/causticizer white liquor</u>

It is often desirable for control applications to obtain liquor samples directly from the slaker or causticizer for analysis. This liquor contains 8-10% by weight suspended calcium carbonate mud solids, which must be removed prior to analysis. The level of solids loading present in this liquor is too high to be introduced immediately to the filter circuit since severe plugging of the filter element would result. The purpose of the mud separation unit is to remove the bulk of the solids from the liquor and yield

a "clear" liquor containing 1% or less suspended mud solids. This "clear" liquor is filterable and becomes the liquor supply to the filter circuit. It should be noted that the mud separation unit in no way interferes with subsequent operation of the analyzer system. The filter, sample, reactor, and gas chromatograph circuits operate exactly as they do when no mud separation circuit is utilized. The mud separation circuit merely ensures that an acceptable liquor sample is provided to the filter circuit.

The best method of mud separation has been found to involve the use of a continuous settling cone. This device receives unclarified liquor from the slaker or causticizer, separates the mud from the liquor, returns the mud to the slaker or causticizer, and supplies a continuous "clear" liquor supply to the filter circuit. The advantages of this apparatus and method are simplicity, reliability, ease of operation and a fresh, uninterrupted supply of liquor to the filter circuit so that operation of the filter circuit is not disturbed.

The settling cone itself is a nonmechanical thickener of a type commonly used for continuous liquid-solid separations in low volume applications. The details of the construction and operation of these units are well known and will not be given in detail here; but may be found in Perry, J. H. (Ed.) Chemical Engineers Handbook, 3rd Ed., McGraw-Hill Book Co., Inc. New York, 1950, pp. 940-941. The mud separation unit should be designed for a capacity that will deliver a desirable flow of "clear" liquor (approximately 2-3 liters/minute) to the filter circuit.

The following description is of the mud separation circuit shown in Figure 4. The circuit consists of the following components:

Major components

T1 - Continuous settling cone.

T2 - Clear liquor tank.

SP1 - Unclarified liquor supply pump from unclarified liquor supply line L39 to unclarified liquor supply line L40.

SP2 - Clear liquor supply pump in filter circuit liquor supply line L29.

B1 - Bustle pipe and launder ring apparatus from settling cone T1 to clear liquor supply line L43.

Lines

L29 - Liquor supply line to the filter circuit.

L39 - Unclarified liquor supply line from slaker (or causticizer) to unclarified liquor supply pump SP1.

L40 - Unclarified liquor supply line from unclarified liquor supply pump SP1 to junction of settling cone inlet line L41 and settling cone bypass line L42.

L41 - Settling cone inlet line from unclarified liquor supply line L40 to settling cone T1.

L42 - Settling cone bypass line from unclarified liquor supply line L40 to slaker (or causticizer) return line L50.

L43 - Clear liquor supply line from bustle pipe/launder ring apparatus B1 to junction of clear liquor tank inlet line L44 and clear liquor tank bypass line L46.

L44 - Clear liquor tank inlet line from clear liquor supply line L43 to clear liquor tank T2.

L45 - Clear liquor tank overflow line from clear liquor tank T2 to clear liquor bypass/overflow line L48.

L46 - Clear liquor tank bypass line from clear liquor supply line L43 to clear liquor bypass/overflow line L48.

L47 - Clear liquor tank outlet line from clear liquor tank T2 to junction of filter circuit liquor supply line L29 and clear liquor tank drain line L51.

L48 - Clear liquor tank bypass/overflow line from junction of clear liquor tank bypass line L46 and clear liquor tank overflow line L45 to slaker (causticizer) return line L50.

L49 - Settling cone mud discharge line from settling cone T1 to slaker (causticizer) return line L50.

L50 - Slaker (causticizer) return line returning flows from clear liquor tank bypass/overflow line L48, mud discharge line L49, and settling cone bypass line L42 to the slaker (or causticizer).

L51 - Clear liquor tank drain line from clear liquor tank outlet line L47 to return line L50.

L52 - Water flush line from mill water supply to unclarified liquor supply line L39.

Operating and repair valves (manually operable)

V30 - Settling cone inlet valve in settling cone inlet line L41. Two positions: open, closed.

V31 - Settling cone bypass valve in settling cone bypass line L42. Two positions: open, closed.

V32 - Clear liquor tank bypass valve in clear liquor tank bypass line L46. Two positions: open, closed.

V33 - Clear liquor tank inlet valve in clear liquor tank inlet line L44. Two positions: open, closed.

V34 - Clear liquor tank outlet valve in filter circuit liquor supply line L29. Two positions: open, closed.

V35 - Clear liquor tank drain valve in clear liquor tank drain line L51. Two positions: open, closed.

V36 - Water flush valve in water flush line L52. Two positions: open, closed.

V37 - Unclarified liquor supply valve in unclarified liquor supply line L39. Two positions: open, closed.

The mud separation unit has five modes of operation, these being the normal operating mode, the clear liquor tank bypass mode, the settling cone bypass mode, the circuit shutdown/water flush mode, and the circuit shutdown/standby mode.

Normal operating mode

The first mode is the normal operating mode. The circuit will normally remain in this mode. The circuit will be removed from this mode only as necessitated by the need for repairs to the mud separation or filter circuits, or upon shutdown of the slaking/causticizing process.

Major parts involved

T1 - Continuous settling cone.

T2 - Clear liquor tank.

SP1 - Unclarified liquor supply pump/on.

SP2 - Clear liquor supply pump/on.

B1 - Bustle pipe/launder ring apparatus.

Lines involved

L29 - Liquor supply line to filter circuit.

L39 - Unclarified liquor supply line.
L40 - Unclarified liquor supply line.
L41 - Settling cone inlet line.
L43 - Clear liquor supply line.
L44 - Clear liquor tank inlet line.
L45 - Clear liquor tank overflow line.
L48 - Clear liquor tank bypass/overflow line.
L49 - Settling cone mud discharge line.
L50 - Slaker (causticizer) return line.

Operating valves/position

V30 - Settling cone inlet valve/open.
V31 - Settling cone bypass valve/closed.
V32 - Clear liquor tank bypass valve/closed (or throttled). May be throttled partially open when circuit is in operation in order to direct some clear liquor to the return line L50 to ensure that L50 does not become plugged.
V33 - Clear liquor tank inlet valve/open.
V34 - Clear liquor tank outlet valve/open.
V35 - Clear liquor tank drain valve/closed.
V36 - Water flush valve/closed.
V37 - Unclarified liquor supply valve/open.

Flow

Unclarified liquor

From slaker (or causticizer) through V37 through L39 through SP1 through L40 through V30 through L41 into T1.

Clear liquor

From T1 through B1 through L43 through V33 through L44 into T2 through L47 through V34 through SP2 through L29.

Mud

From T1 through L49 through L50 to slaker (or causticizer).

Time

The time will vary. The circuit will normally be in this mode, being removed from this mode only for maintenance of this circuit or the filter circuit or upon shutdown of the slaking and causticizing process.

Clear liquor tank bypass mode

The second mode is the clear liquor tank bypass mode. This mode is utilized when it is necessary to stop the flow of clear liquor to the clear liquor tank. This may be necessitated by the need for repairs to this part of the circuit, or by the need for repairs to the filter circuit which require that the flow of clear liquor to the filter circuit be stopped.

Major components involved

T1 - Continuous settling cone.
T2 - Clear liquor tank.
SP1 - Unclarified liquor supply pump/on.
SP2 - Clear liquor supply pump/off.
B1 - Bustle pipe/launder ring apparatus.

Lines involved

L39 - Unclarified liquor supply line.
L40 - Unclarified liquor supply line.
L41 - Settling cone inlet line.
L43 - Clear liquor supply line.
L46 - Clear liquor tank bypass line.
L47 - Clear liquor tank outlet line.
L48 - Clear liquor tank bypass/overflow line.
L49 - Settling cone mud discharge line.
L50 - Slaker (or causticizer) return line.
L51 - Clear liquor tank drain line.

Operating valves/position

V30 - Settling cone inlet valve/open.
V31 - Settling cone bypass valve/closed.
V32 - Clear liquor tank bypass valve/open.
V33 - Clear liquor tank inlet valve/closed.
V34 - Clear liquor tank outlet valve/closed
V35 - Clear liquor tank drain valve/open.
V36 - Water flush valve/closed.
V37 - Unclarified liquor supply valve/open.

Flows

Unclarified liquor

From slaker or causticizer through V37 through L39 through SP1 through L40 through V30 through L41 into T1.

Clear liquor

From T1 through B1 through L43 through V32 through L46 through L48 through L50 to slaker or causticizer.

From T2 through L47 through L35 through L51 through L50 into slaker or causticizer.

Mud

From T1 through L49 through L50 to slaker or causticizer.

Time

Varies as required to repair maintenance problem necessitating clear liquor tank bypass.

Settling Cone Bypass Mode

The third mode is the settling cone bypass mode. This mode is utilized when it is necessary to stop operation of the settling cone in order to repair this part of the circuit. The flow of clear liquor will be interrupted in this mode and there will be no sample flow to the filter circuit and analyzer.

Major components involved

SP1 - Unclarified liquor supply pump/on.

SP2 - Clear liquor supply pump/off.

Lines involved

L39 - Unclarified liquor supply line.

L40 - Unclarified liquor supply line.

L42 - Settling tank bypass line.

L47 - Clear liquor tank outlet line.

L50 - Slaker or causticizer return line.

L51 - Clear liquor tank drain line.

Operating valves/position

V30 - Settling tank inlet valve/closed.

V31 - Settling tank bypass valve/open.

V32 - Clear liquor tank bypass valve/closed.

V33 - Clear liquor tank inlet valve/open.

V34 - Clear liquor supply valve/open.

V35 - Clear liquor tank drain valve/open.

V36 - Water flush valve/open.

V37 - Unclarified liquor supply valve/open.

Flows

Unclarified liquor

From slaker or causticizer through V37 through L39 through SP1 through L40 through V31 through L42 through L50 to slaker or causticizer.

Time

Varies as needed to complete maintenance repairs necessitating bypass of settling cone.

Circuit Shutdown/Water Flush Mode

The fourth mode is the circuit shutdown/water flush mode. This mode is used when it is necessary to entirely shut down the circuit for maintenance or in response to a shutdown of the slaking/causticizing process. The flow of unclarified liquor to the system is stopped and all lines and major parts are flushed with water to ensure that they are clean and unplugged.

Major components involved

T1 - Settling cone.
T2 - Clear liquor tank.
SP1 - Unclarified liquor supply pump/on.
SP2 - Clear liquor supply pump/on.
B1 - Bustle pipe/launder ring.

Lines involved

L40 - Unclarified liquor supply line.
L41 - Settling tank inlet line.
L42 - Settling tank bypass line.
L43 - Clear liquor supply line.
L44 - Clear liquor tank inlet line.
L45 - Clear liquor tank overflow line.
L46 - Clear liquor tank bypass line.
L47 - Clear liquor tank outlet line.
L48 - Clear liquor tank bypass/overflow line.
L49 - Settling cone mud discharge line.
L50 - Return line to slaker or causticizer.
L51 - Clear liquor tank drain line.
L52 - Water flush line.

Operating valves/position

V30 - Settling cone inlet valve/open.
V31 - Settling cone bypass valve/open.
V32 - Clear liquor tank bypass valve/open.
V33 - Clear liquor tank inlet valve/open.
V34 - Clear liquor tank outlet valve/open.
V35 - Clear liquor tank drain valve/open.
V36 - Water flush valve/open.
V37 - Unclarified liquor supply valve/closed.

Flow

Water

Through L52 through V36 through L39 through SP1 through L40 through:

V31 through L42 through L50 into slaker or causticizer.

V30 through L41 into T1.

From T1 through L49 through L50 into slaker or causticizer.

From T1 through B1 through L43 through:

V32 through L46 through L48 through L50 into slaker or causticizer.

V33 through L44 into T2 through L47 through:

V34 through SP2 through L29.

V35 through L51 through L50 into slaker or causticizer.

Time

15 minutes or as needed to completely flush circuit with water.

Note

This operation, as described, will completely flush the entire circuit with water. Selected valves may be closed as desired to direct wash water only through selected lines and parts of the circuit. It is not always necessary or desirable to flush the entire circuit.

Circuit Shutdown/Standby Mode

The fifth mode is the circuit shutdown/standby mode. This mode is used after the circuit has been flushed with water. The circuit is in a "standby" condition and will remain in this condition until restarted.

Major components involved

All components are in "standby." All tanks are drained and all pumps are off.

Lines

All lines have been flushed and drained and remain in a standby mode.

Operating valves/position

V30 - Settling tank inlet valve/open.
V31 - Settling tank bypass valve/closed.
V32 - Clear liquor tank bypass valve/closed.
V33 - Clear liquor tank inlet valve/open.
V34 - Clear liquor supply valve/open.
V35 - Clear liquor tank drain valve/closed.
V36 - Water flush valve/closed.
V37 - Unclarified liquor supply valve/closed.

Flow

No flow in circuit once tanks and lines empty and drain.

To restart the circuit and return to the first or normal operating mode, the unclarified liquor supply valve V29 is opened and pumps SP1 and SP2 are turned on. The circuit will then resume normal operation. The circuit should be started and be running at least 30 minutes prior to starting the rest of the analyzer system in order to ensure that all tanks have been filled and the circuit has reached equilibrium.

Sampling circuit

The purpose of the sampling circuit is to obtain a measured liquor sample and a measured amount of acid, to hold them separately until the reactor can receive them, and to transport them to the reactor. It has two main sections, a sample valve and an associated sample loop shown in the upper central part of Figure 1, and an acid section shown in the right hand side of Figure 1. The sample loop obtains a 10 cc sample of the filtered liquor and the acid pump obtains a 50 cc sample of 10% sulfuric acid by volume (approximately 2.2 N). The acid pump strokes to deliver a full 50 cc of acid but only 40 cc goes to reactor. The rest is left in the sample loop SL2 and is washed out when fresh liquor displaces the acid in the liquor sampling mode.

It has the following components:

Major components

SL2 - Sample loop for obtaining a 10 cc filtered liquor sample. It is connected to the ports P5 and P6 of the sample valve V14.

AP1 - The air piston for operating the piston in the positive displacement acid pump AP2. Two positions: position one (acid in or fill) (1F); position two (acid out or transfer) (2T).

AP2 - Positive displacement acid pump for obtaining a 50 cc sample of 10% sulfuric acid. Two positions: position one (acid fill and standby) (1F); position two (acid out or transfer) (2T).

Lines

L9 - Antiflocculant line from the antiflocculant supply to the acid supply line L20.

L14 - Air line from the air supply line L27 to the valve V11.

L15 - Air line from the valve V11 to the port P1 of the sample valve V14 for supplying air to move the sample valve V14 to position one (sampling) (1S).

L16 - Air line from the valve V11 to the port P2 of the sample valve V14 for supplying air to move the sample valve V14 to position two (transferring) (2T).

L17 - Sample line from the port P4 of the sample valve V14 to the port R9 of the reactor R1.

L19 - Acid line from the acid line L21 to the port P3 of the sample valve V14.

L20 - Acid supply line from the acid supply to the acid line L21.

L21 - Acid line from the juncture of acid lines L19 and L20 to the acid pump AP2.

L22 - Sample line from the filter system to the port P8 of the sample valve V14.

L23 - Sample line from the port P7 of the sample valve V14 to the sewer.

L24 - Air line from the valve V17 to the inner side of the piston in AP1 to move the piston outwardly to position one (acid fill) (1F).

L25 - Air line from the valve V17 to the outer side of the piston in AP1 to move the piston inwardly to position two (acid transfer) (2T).

L26 - Air line from the air supply line L27 to the valve V17.

L27 - Air supply line.

Valves

Operating valves

V11 - Solenoid operated air valve connecting the air line L14 to either the air line L15 or the air line L16 to position the sample valve V14. Two positions: position one (sampling) (1S) - the air line L14 connected to the air line L15; position two (transferring) (2T) - the air line L14 connected to the air line L16.

V14 - Air operated sample valve has two operational ports.

P1 - Connected to the air line L15 to allow air to move the valve to position one (sampling), and

P2 - Connected to the air line L16 to allow air to move the valve to position two (transferring).

And six sample ports:

P3 - Connected to the acid line L19,

P4 - Connected to the sample line L17,

P5 - Inlet to the sample loop SL2,

P6 - Outlet from the sample loop SL2,

P7 - Connected to the sewer line L23,

P8 - Connected to the sample line L22.

It has two positions:

Position one (sampling) (1S) - receiving the sample from the filter circuit into the sample loop SL2. Connects ports P5, P6, P7 and P8.

Position two (transferring) (2T) - sending the sample from the sample loop SL 2 to the reactor R1. Connects ports P3, P4, P5 and P6 and sends acid charge from AP2 through sample loop SL2 to reactor R1.

V17 - Solenoid operated air valve connecting air line L26 to either the air line L24 or the air line L25. Two positions: position one (acid fill) (1F): the air line L26 connected to the air line L25; position two (acid transfer) (2T): the air line L26 connected to the air line L24.

Check valves

V12 - Check valve in the sample line L17 prevents material or gas from returning through the line L17 from the reactor R1 to the sampling circuit.

V15 - Check valve in the acid line L19 prevents backflow of acid from L19 through L20 into AP2 during the acid pump fill mode.

V16 - Check valve in the acid supply line L20 prevents backflow of acid through the acid supply line L20 during the acid transfer mode.

Pressure regulation valves

AR2 - Pressure regulation valve in the air line L26.

AR3 - Pressure regulation valve in the air line L14.

The sample valve and its associated sample loop receives and holds a measured liquor sample. The acid system receives and holds a measured amount of acid separate from the liquor sample. These are held until the reactor can accept the sample and the acid. The circuit then transports the sample, followed by the acid, to the reactor R1. During this latter step, the acid passes through the sample loop SL2. This accomplishes two objectives: (1) the sample is transported to the reactor assembly by the acid and (2) the sample loop is cleaned by the acid during the injection. After the transfer some acid remains in the loop and will dissolve any residue that may remain in the loop. Cleaning the sample loop before each liquor analysis is important because the liquor being handled tends to crystallize out on any surfaces with which it comes in contact. During the

next sample reception, the sample is circulated through the sample loop SL2 and out of the system through line L23. This requires 60 to 100 seconds to ensure that all of the acid and any residue that may be present is removed from the sample loop, and that the new sample is a representative sample of the liquor currently being utilized by the process.

The sampling circuit has several operating modes. In many of these modes the valving arrangement is the same.

An initial acid flush cycle (Modes 1-4) is performed at start-up to ensure that the sample system is clean and filled with acid before sample analysis begins. At start-up, there may or may not be a sample in the sample loop depending upon the status of the sample system at shutdown.

Standby mode (Standby 1)

The first mode is a standby mode in which there is acid or liquor in the sample loop SL2, depending on the status of the sample circuit at shutdown.

Major components involved

SL2 - Sample loop/filled with 10 cc of acid or liquor.

AP1 - Air operated piston for operating the piston in the acid pump/position one (acid fill) (1F).

AP2 - Acid pump/position one (acid fill) (1F).

Lines involved

L14 - Air line from the air supply line L27 to the valve V11.

L15 - Air line from the valve V11 to the port P1 of the sample valve V14.

L24 - Air line from the valve V17 to the inner side of the piston in AP1.

L26 - Air line from the air supply line L27 to the valve V17.

L27 - Air supply line.

Valves involved

Operating valves/position

V11 - Solenoid operated air valve/position one (sampling) (1S): connecting the air lines L14 and L15.

V14 - Air operated sample valve/position one (sampling) (1S): connecting the ports P5, P6, P7 and P8.

V17 - Solenoid operated air valve/position one (acid fill) (1F): connecting the air lines L26 and L24.

Check valves

V15 - Check valve in the acid line L19 holds acid in the line L19.

V16 - Check valve in the acid supply line L20 holds acid in the acid lines L20 and L21.

Pressure regulation valves

AR2 - Pressure regulation valve in the air line L26.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

L27 through AR3 through L14 through V11 through L15 through P1 into V14.

L27 through AR2 through L26 through V17 through L24 into AP1.

Liquor

No flow.

Sample valve repositioning mode (Reposition 1)

The second mode is a sample valve repositioning mode. The sample valve is moved from the sample receiving position to the sample transferring position.

Major components involved

SL2 - Sample loop/10 cc of acid present.

AP1 - Air operated piston for operating the piston in the acid pump/position one (acid fill) (1F).

AP2 - Positive displacement acid pump/position one (acid fill) (1F).

Lines involved

L14 - Air line from the air supply line L27 to the valve V11.

L16 - Air line from the valve V11 to the port P2 of the sample valve V14.

L24 - Air line from the valve V17 to the inner side of the piston in AP1.

L26 - Air line from the air supply line L27 to the valve V17.

L27 - Air supply line.

Valves involved

Operating valves/position

V11 - Solenoid operated air valve/position two (transferring) (2T): connecting the air lines L14 and L16.

V14 - Air operated sample valve/position two (transferring) (2T): connecting the ports P3, P4, P5 and P6.

V17 - Solenoid operated air valve/position one (acid fill) (1F): connecting the air lines L26 and L25.

Check valves

V15 - Check valve in the acid line L19 holds acid in the line L19.

V16 - Check valve in the acid supply line L20 holds acid in the acid lines L20 and L21.

Pressure regulation valves

AR2 - Pressure regulation valve in the air line L26.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

L27 through AR3 through L14 through V11 through L16 through P2 into V14.

L27 through AR2 through L26 through V17 through L24 into AP1.

Time

5 seconds or as needed to ensure V14 has completed switching.

Acid transferring mode (Transfer 1)

The third mode is a transfer mode in which the acid pump forces the 50 cc of acid in the acid pump AP2 through the sample loop SL2 and into the reactor. An initial flushing of the system with acid is performed to ensure that the system is cleaned and filled with acid before sample analysis commences.

Major components involved

SL2 - Sample loop.

AP1 - Air operated piston for operating the piston in the acid pump/position two (acid transfer) (2T).

AP2 - Positive displacement acid pump/position two (acid transfer) (2T).

Lines involved

L14 - Air line from the air supply line L27 to the valve V11.

L16 - Air line from the valve V11 to the port P2 of the sample valve V14.

L17 - Sample line from the port P4 of the sample valve V14 to the port R9 of the reactor R1.

L19 - Acid line from the acid line L21 to the port P3 of the sample valve V14.

L21 - Acid line from the acid pump AP2 to the acid line L19.

L25 - Air line from the valve V17 to the outer side of the piston in AP1.

L26 - Air line from the air supply line L27 to the valve V17.

L27 - Air supply line.

Valves involved

Operating valves/position

V11 - Solenoid operated air valve/position two (transferring) (2T): connecting the air lines L14 and L16.

V14 - Air operated sample valve/position two (transferring) (2T): connecting the ports P3, P4, P5 and P6.

V17 - Solenoid operated air valve/position two (acid transfer) (2T): connecting the air lines L26 and L24.

Check valves

V12 - Check valve in the sample line L17 prevents the liquor and acid from returning to the sample circuit once it has entered the reactor.

V15 - Check valve in the acid line L19 allows acid to flow from AP2 through L21 through L19 into V14.

V16 - Check valve in the acid line L20 prevents acid from returning to the acid supply system when AP2 transfers the acid.

Pressure regulation valves

AR2 - Pressure regulation valve in the air line L26.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

L27 through AR3 through L14 through V11 through L16 through P2 into V14.

L27 through AR2 through L26 through V17 through L25 into AP1 to move piston upwardly.

Liquid

AP2 through L21 through V15 through L19 through P3 through P5 through SL2 through P6 through P4 through V12 through L17 into R1.

Time

30 seconds or as needed to ensure AP2 has completed its stroke.

Sample valve repositioning mode 2 (Reposition 2)

The fourth mode is a second sample valve repositioning mode to move the sample valve from position two (transferring) to position one (sampling), and to move the acid pump from position two (acid transfer) to position one (acid fill) to fill the acid pump with acid and antiflocculant. It is necessary to add antiflocculant to the reaction mixture to prevent flocculation and deposition of sulfur in the reactor. It is best to add a known amount of antiflocculant to each reaction by mixing antiflocculant solution with acid when the acid pump refills.

By proper choice of antiflocculant storage concentration and proper sizing of antiflocculant lines L9 and acid supply line L20, the proportions of acid and antiflocculant drawn into the acid pump AP2 will be such as to ensure a desirable concentration of antiflocculant in the reaction mixture. Sufficient turbulence exists in L20, L21 and AP2 during the acid fill step to ensure adequate dissolution of antiflocculant in the acid.

Major components involved

SL2 - Sample loop/approximately 10 cc acid.

AP1 - Air operated piston for operating the piston in the acid pump/position one (acid fill) (1F).

AP1 - Positive displacement acid pump/position one (acid fill) (1F).

Lines involved

L9 - Antiflocculant supply line from antiflocculant storage to acid supply line L20.

L14 - Air valve from the air supply line to the valve V11.

L15 - Air line from the valve V11 to the port P1 of the sample valve V14.

L20 - Acid supply line from the acid supply to the line L21.

L21 - Acid line from the acid supply line L20 to the acid pump AP2.

L24 - Air line from the valve V17 to the inner side of the piston in AP1.

L26 - Air lines from the air supply line L27 to the valve V17.

L27 - Air supply line.

Valves involved

Operating valves/position

V11 - Solenoid operated air valve/position one (sampling) (1S).

V14 - Air operated sample valve/position one (sampling) (1S): connecting the ports P5, P6, P7 and P8.

V17 - Solenoid operated air valve/position one (acid fill) (1F): connecting the air lines L26 and L25.

Check valves

V15 - Check valve in the acid line L19 prevents backflow of acid from L19 through L21 into AP2.

V16 - Check valve in the acid supply line L20 allows acid to flow from L20 through L21 into AP2.

Pressure regulation valves

AR2 - Pressure regulation valve in the air line L26.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

L27 through AR3 through L14 through V11 through L15 through P1 into V14.

L27 through AR2 through L26 through V17 through L24 into AP1.

Acid

L20 through V16 through L21 into AP2.

Antiflocculant

L9 through L20 through V16 through L21 into AP2.

Time

5 seconds

Note: Time not really important - a great excess of time (approximately 12 minutes for the system described) is available for the pump to fill and valve to switch.

Standby mode (Standby 2)

The fifth mode is a second standby mode (Standby 2) in which the sample valve waits to receive a sample from the filter circuit. It is identical to the first mode (Standby 1) and will not be given in detail again. Its time is 12 minutes, but may change depending on the operation of a particular system.

Sample collecting mode (Sample)

The sixth mode is a sample collecting mode in which a sample is collected from the filter circuit.

Major components involved

SL2 - Sample loop/initially filled with 10 cc acid from last sample transfer mode.

AP1 - Air operated piston for operating the piston in the acid pump/position one (acid fill) (1F).

AP2 - Positive displacement acid pump/position one (acid fill) (1F).

Lines involved

L14 - Air line from the air supply line L27 to the valve V11.

L15 - Air supply line from the valve V11 to the port P1 of the sample valve V14.

L22 - Liquor sample line from the filter system to the port P8 of the sample valve V14.

L23 - Sample line from the port P7 of the sample valve V14 to the sewer.

L24 - Air line from the valve V17 to the inner side of the piston in AP1.

L26 - Air line from the air supply line L27 to the valve V17.

L27 - Air supply line.

Valves involved

Operating valves/position

V11 - Solenoid operated air valve/position one (sampling) (1S): connecting the air lines L14 and L15.

V14 - Air operated sample valve/position one (sampling) (1S): connecting the ports P5, P6, P7 and P8.

V17 - Solenoid operated air valve/position one (acid fill) (1F): connecting the air lines L26 and L25.

Check valves

V15 - Check valve in the acid line L19 holds the acid in the line L19.

V16 - Check valve in the acid supply line L20 holds the acid in the lines L20 and L21.

Pressure regulation valves

AR2 - Pressure regulation valve in the air line L26.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

L27 through AR3 through L14 through V11 through L15 through P1 into V14.

L27 through AR2 through L26 through V17 through L24 into AP1.

Liquor

L22 through P8 through P5 through SL2 through P6 through P7 through L23.

Time

60 seconds or as needed to ensure complete flushing and filling of sample loop with a fresh liquor sample.

Standby mode (Standby 3)

The seventh mode is a third standby mode (Standby 3) in which the sample circuit waits for the reactor circuit to receive the sample. It is identical to the first and fifth modes (Standby 1 and Standby 2) and will not be given in detail. The sample loop is filled with liquor rather than acid at this stage.

Sample valve repositioning mode (Reposition 3)

The eighth mode is a third sample valve repositioning mode (Reposition 3) in which the sample valve V14 is moved from position one (sampling) to position two (transferring). It is identical to the second mode (Reposition 1) and will not be given in detail. Its time is the same as Reposition 1.

Acid transferring mode (Transfer 2)

The ninth mode is a second transfer mode (Transfer 2) in which the acid pump forces the 50 cc of acid through the sample loop and into the reactor. This carries the sample into the reactor also. Acid remains in the sample loop to clean the sample loop of any material that may have coated on the tubing during the seventh mode (Standby 3). This acid and the residue will be removed from the system during the next sample collecting mode. It is identical in operation to the third mode (Transfer 1) and will not be given in detail.

Sample valve repositioning mode (Reposition 4)

The tenth mode is a fourth repositioning mode (Reposition 4) in which the sample valve V14 is moved from position two (transferring) to position one (sampling) and the acid pump AP2 is filled with acid and antiflocculant. It is identical to the fourth mode (Reposition 2) and its time is the same.

Reactor circuit

The reactor is shown in Figures 5 and 6 and the reactor circuit is shown in the bottom left hand section of Figure 1.

As may be seen in Figure 5, the reactor R1 has a reactor compartment R2 which is defined by a cover member R3, sidewalls R4 and a base R5. The cover member R3 has four ports: R6 for the vent gas from the reactor to the sewer line, R7 for the wash water to the reactor, R8 both for the reactor gas from the reactor to the gas chromatograph and for gas under pressure to pressurize the reaction chamber, and R9 for the sample and acid to the reactor. The base R5 defines the bottom R10 of the chamber R2. The bottom R10 is sloped toward the central outlet valve V13 so that the reaction chamber R2 may be washed and drained easily after each reaction. The magnetic spin bar R13 provides turbulence and mixing of the reaction mixture. The base R5 rests on a pressure chamber R11 and pressure within the chamber R11 is maintained by the rubber diaphragm R12

between the base R5 and the pressure chamber R11. Air enters the pressure chamber R11 through air line L1 and the air pressure holds the valve V13 in its upper closed position to maintain liquid within the reaction chamber R2. When the air pressure is bled from the line L1, the valve V13 drops into its lower position allowing the reaction chamber R2 to be drained. The liquid goes into outlet line L18 to be sewered or otherwise treated.

The reactor circuit has the following components:

Major components

R1 - Reactor

M1 - Magnetic spin bar driver for reactor mixer.

Lines

L1 - Air line from the valve V10 to the reactor outlet pressure chamber R11.

L2 - Line to the gas chromatograph GC.

L2A - Line between the reactor gas line L6 and the gas chromatograph GC.

L2B - Line between the reactor pressurization line L10 and the line L2A.

L3 - Air line between the air supply line L27 and the line L11.

L4 - Water supply line between the water supply and the port R7 of the reactor R1.

L5 - Vent line from the port R6 of the reactor R1 to the sewer.

L6 - Reaction gas line from the line L13 to the line L2A.

L7 - Air line between air line L14 and the spin bar driver M1.

L8 - Reactor pressurization line between the reactor pressurization line L10 and the reactor line L13.

L10 - Reactor pressurization line between air supply line L27 and lines L8 and L2B.

L11 - Connecting line between the air line L3 and the gauge line L12, and the reactor gas line L6, the air pressure line L8 and the reactor line L13.

L12 - Gauge line between the air line L3 and the connecting line L11, and the gauge protector G1 and the pressure gauge G2.

L13 - Reactor line between the port R8 of the reactor R1 and the juncture of the reactor gas line L6, the reactor pressurization line L8 and the connecting line L11.

L14 - Air line between the air supply line L27 and the valve V10.

L17 - Sample line between the sample valve V14 and the port R9 of the reactor R1.

L18 - Outlet line from the valve V13 of the reactor R1.

Valves

Operating valves (solenoid operated)

V3 - Valve in the air line L3. Two position: open; closed.

V4 - Valve in the water line L4. Two positions: open; closed.

V5 - Valve in the vent line L5. Two positions: open; closed.

V6 - Valve in the reaction gas line L6. Two positions: open; closed.

V8 - Valve in the reactor pressurization line L8. Two positions: open; closed.

V10 - Valve between the air line L14 and the air line L1. Two positions: open; closed.

Operating valves (air operated)

V13 - Outlet valve in the reactor R1 between the reaction chamber R2 and the outlet line L18. It is operated by air pressure from the line L1. Two positions: closed when the air is on; open when the air is off.

Check valves

V12 - Check valve in the sample line L17 preventing either the sample, the reaction gas or air from flowing back through the sample line L17.

Pressure regulation valves

AR1 - Pressure regulation valve in the air line L1.

AR3 - Pressure regulation valve in the air line L14.

AR4 - Pressure regulation valve in the air line L3.

AR5 - Pressure regulation valve in the reactor pressurization line L10.

Repair valves (normally open, manually operable)

V7 - Repair valve in the air line L7.

Ports

R6 - Port in the reactor R1 for the vent line L5.

R7 - Port in the reactor R1 for the water line L4.

R8 - Port in the reactor R1 for the reactor line L13.

R9 - Port in the reactor R1 for the sample line L17.

The operating sequence of the reactor is as follows:

(1) The reactor is cleaned:

(a) The reactor is drained.

(b) The reactor is filled with water.

(c) The reactor is again drained.

(d) The reactor is again filled with water.

(e) The reactor is again drained.

(f) The reactor is again filled with water.

(g) The reactor is again drained.

(2) The reactor is vented for 5 seconds, then resealed.

(3) The acid and sample are placed in the reactor and the reaction starts.

(4) After approximately 11 minutes, the reactor is placed under pressure using a precise air pressure regulator. This is important if a direct relationship between gas chromatograph output and liquor concentration is to be obtained. The final reactor pressure should be about 2 psi above the highest total reactor pressure resulting from the sum of all the partial pressures or the expected components or 26 psi above the ambient pressure. This is to compensate for the dependence of reactor pressure on liquor concentration which would provide an incorrect reading if there was no compensation.

(5) The reaction is allowed to go to completion.

(6) The reaction gas is transferred to the gas chromatograph. The time of transfer must be long enough to obtain a representative sample of gas in the sample loop SL1 of the gas chromatograph. This usually requires 40-50 seconds.

The cycle takes approximately 19 minutes, but will vary according to the characteristics of each individual system.

Standby mode (Standby)

The first mode of the reactor circuit is a standby mode in which the reactor is waiting to receive the sample. It usually occurs only at start-up. The reactor contains whatever was present in it at shutdown. This can be the old reaction mixture, wash water, etc.

Major components involved

R1 - Reactor

Lines involved

L1 - Air line from the valve V10 to the valve V13.

L14 - Air line from the air supply line L27 to the valve V10.

L27 - Air supply line.

Valves involved

Operating valves/position

V3 - Valve in the air line L3/closed.

V4 - Valve in the water line L4/closed.

V5 - Valve in the vent line L5/closed.

V6 - Valve in the reaction gas line L6/closed.

V8 - Valve in the air pressure line L8/closed.

V10 - Valve between the air lines L14 and L1/open.

V13 - Outlet valve in the reactor R1/closed.

Pressure regulation valves

AR1 - Pressure regulation valve in the air line L1.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

L27 through AR3 through L14 through V10 through L1 through AR1 into R11 to hold V13 closed.

Vent mode (Vent)

The second mode is a vent mode. The reactor is vented when the sample valve V14 is repositioned from position one (sampling) to position two (transferring). This allows the pressure in the reaction chamber to reach atmospheric pressure prior to sample injection. The gas in the reactor contains, at most, minor amounts of carbon dioxide and hydrogen sulfide.

Major components involved

R1 - Reactor

Lines involved

L1 - Air line from the valve V10 to the chamber R11 of the reactor R1.

L5 - Vent line from the port R6 of the reactor R1 to the atmosphere.

L14 - Air line between the air supply line L27 and the valve V10.

L27 - Air supply line.

Valves involved

Operating valves/position

V3 - Valve in the air line L3/closed.

V4 - Valve in the water line L4/closed.

V5 - Valve in the vent line L5/open.

V6 - Valve in the reaction gas line L6/closed.

V8 - Valve in the pressure line L8/closed.

V10 - Valve between the air lines L14 and L1/open to hold the outlet valve V13 of the reactor R1 closed.

V13 - Outlet valve from the reactor R1/closed.

Pressure regulation valves

AR1 - Pressure regulation valve in the air line L1.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

R1 through R6 through V5 through L5 to vent line to sewer. L27 through AR3 through L14 through V10 through L1 through AR1 into R11 to hold V13 closed.

Time

5 seconds as needed for air in reactor to reach equilibrium with atmospheric pressure. In the vent mode prior to the introduction of the sample, the vent mode must end prior to introduction of sample into reactor to ensure no loss of reaction gas products.

Drain mode (Drain)

The third mode is a reactor drain mode. During the washing cycle the reactor is drained either of reaction products or of wash water.

Major components involved

R1 - Reactor

Lines involved

L1 - Air line from the valve V10 to the outlet valve V13 of the reactor R1.

L3 - Air line from the air supply line L27 to the connecting line L11.

L11 - Connecting line from the air line L3 to the reactor line L13.

L13 - Reactor line from the connecting line L11 to the port R8 of the reactor R1.

L18 - Outlet line from the reactor R1.

L27 - Air supply line.

Valves involved

Operating valves/position

V3 - Valve in the air line L3/open.

V4 - Valve in the water line L4/closed.

V5 - Valve in the vent line L5/closed.

V6 - Valve in the reaction gas line L6/closed.

V8 - Valve in the air pressure line L8/closed.

V10 - Valve between the air lines L14 and L1/closed to bleed air from the line L1 to open the valve V13.

V13 - Outlet valve of the reactor R1/open to drain the reactor through the outlet line L18.

Check valves

V12 - Check valve in the sample line L17 prevents air from escaping through the sample line L17.

Pressure regulation valves

AR4 - Pressure regulation valve in the air line L3.

Flow

Air

No flow in line L1.

L27 through AR4 through L3 through V3 through L11 through L13 through R8 into R1.

Liquid

R1 through V13 through L18.

Time

10 seconds or as needed to completely drain reactor.

Fill mode (Fill)

The fourth mode is the reactor fill mode. During the wash cycle, the reactor is filled with wash water.

Major components involved

R1 - Reactor

Lines involved

L1 - Air line from the valve V10 to the chamber R11 of the reactor R1.

L4 - Water line between the water supply and the port R7 of the reactor R1.

L5 - Vent line from the port R6 of the reactor R1 to the atmosphere.

L14 - Air line from the air supply line L27 to the valve V10.

L27 - Air supply line.

Valve involved

Operating valves/position

V3 - Valve in the air line L3/closed.

V4 - Valve in the water line L4/open.

V5 - Valve in the vent line L5/open.

V6 - Valve in the reaction gas line L6/closed.

V8 - Valve in the air pressure line L8/closed.

V10 - Valve between the air lines L14 and L1/open.

V13 - Outlet valve of the reactor R1/closed.

Check valves

V12 - Check valve in the sample line L17 prevents air from entering the sample circuit.

Pressure regulation valves

AR1 - Pressure regulation valve in the air line L1.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

R1 through R6 through V5 through L5 to vent line to sewer.

L27 through AR3 through L14 through V10 through L1 through AR1 into R11 to hold V13 closed.

Water

L4 through V4 through R7 into R1.

Time

20 seconds or as needed to sufficiently fill reactor with water.

Sample transferring mode (Transfer)

The sixth mode is the sample transferring mode. The sample is received from the sampling circuit.

Major components involved

R1 - Reactor.

Lines involved

L1 - Air line from the valve V10 to the outlet valve 13 of the reactor R1.

L14 - Air line from the air supply line L27 to the valve V10.

L17 - Sample line from the sample circuit to the port R9 of the reactor R1.

L27 - Air supply line.

Valves involved

Operating valves/position

V3 - Valve in the air line L3/closed.

V4 - Valve in the water line L4/closed.

V5 - Valve in the vent line L5/closed.

V6 - Valve in the reaction gas line L6/closed.

V8 - Valve in the air pressure line L8/closed.

V10 - Valve between the air lines L14 and L1/open.

V13 - Outlet valve from the reactor R1/closed.

Check valves

V12 - Check valve in the sample line L17 prevents the sample or reaction gases from returning through line L17.

Pressure regulation valves

AR1 - Pressure regulation valve in the air line L1.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

L27 through AR3 through L14 through V10 through L1 through AR1 into R11 to hold V13 closed.

Liquor

SL2 through V14 through L17 through V12 through R9 into R1.

Acid

AP2 through L21 through V15 through L19 through V14 through SL2 through L17 through V12 through R9 into R1.

Time

30 seconds or as needed to ensure complete transfer of acid and sample.

Reaction mode (Reaction)

The seventh mode is the reaction mode. The reaction between the acid and the sample takes place in the reaction chamber. There are two stages in the reaction mode, reaction 1 and reaction 2. Reaction 2 is the continuation of reaction 1 after pressure has been applied to the reaction chamber and is identical to reaction 1.

Major components involved

R1 - Reactor

Lines involved

L1 - Air line from the valve V10 to the outlet valve V13 of the reactor R1.

L14 - Air line from the air supply line L27 to the valve V10.

L27 - Air supply line.

Valves involved

Operating valves/position

V3 - Valve in the air line L3/closed.

V4 - Valve in the water line L4/closed.

V5 - Valve in the vent line L5/closed.

V6 - Valve in the reaction gas line L6/closed.

V8 - Valve in the air pressure line L8/closed.

V10 - Valve between air lines L14 and L1/open.

V13 - Outlet valve in the reactor R1/closed.

Check valves

V12 - Check valve in the sample line L17 prevents the reaction gas from entering the sample circuit through the sample line L17.

Pressure regulation valves

AR1 - Pressure regulation valve in line L1.

AR3 - Pressure regulation valve in air line L14.

Flow

Air

L27 through AR3 through L14 through V10 through L1 through AR1 into R11 to hold V13 closed.

Time

The total time of the reaction is about 15 minutes. It is divided into the two parts before and after pressure is applied.

Pressurization mode (Pressure)

The eighth mode is a pressurization mode. Eleven minutes after the reaction begins, air pressure is applied through a precise regulator to the reaction chamber to maintain a constant final reactor pressure.

It was decided to pressurize 11 minutes into the reaction, because at this time:

1) the reaction is essentially complete and no further pressure rise is anticipated;

2) four minutes of reaction time remain, which allows the air which has been added in the pressurization step to become well mixed with the reaction gases to yield a homogeneous reaction gas sample at the end of the reaction.

The time of pressurization may be changed as needed in response to the characteristics of individual reactor systems.

The pressurization step was added in response to observations made during the development of the system. In order to make valid comparisons among samples, it is necessary to have a constant final gas pressure. If this is not done, then the experience of our experiments will be repeated. In these experiments, the final gas pressure inside the reactor was allowed to remain at whatever pressure existed due to the release of carbon dioxide and hydrogen sulfide from the reaction. This pressure varied

according to the amounts of sodium carbonate and sodium sulfide in the liquor sample. It was observed that, although an increase in sodium carbonate concentration in the liquor did cause an increase in the carbon dioxide peak area generated by the gas chromatograph, the relationship was not directly proportional. Furthermore, the carbon dioxide peak area was influenced by the amount of Na_2S in the liquor, which resulted in erroneous sodium carbonate measurements due to changes in the sodium sulfide concentration in the liquor. The measurement of sodium sulfide in the liquor was affected in the same manner.

After this was realized, it was decided to adjust the pressure so that there would be the same total moles of gas in the system for each measurement. This can be done by maintaining the reaction gas in the reactor at a constant pressure at the completion of the reaction. The addition of air will act as a diluent, and the total moles of gas will remain fixed among a number of samples. It has been found that the total pressure of air, carbon dioxide and hydrogen sulfide, under the conditions existing in the reactor, will not exceed 24 psi. By adding additional air to obtain a 26 psi pressure, it is possible to obtain gas samples each containing a constant total number of moles of gas. The air has substantially no carbon dioxide or hydrogen sulfide and does not affect the readings for carbon dioxide or hydrogen sulfide generated in the reaction. The peak areas for carbon dioxide and hydrogen sulfide will then be directly proportional to the concentrations of sodium carbonate and sodium sulfide, respectively, in the liquor. Furthermore, sodium carbonate measurements will not be affected by the sodium sulfide concentration in the liquor, nor will the sodium sulfide measurements be affected by the sodium carbonate concentration. The measurements of sodium carbonate and sodium sulfide are then used to control the process.

Major components involved

R1 - Reactor

Lines involved

L1 - Air line between the valve V10 and the outlet valve V13 of the reactor R1.

L8 - Reactor pressurization line between the reactor pressurization line L10 and the reactor line L13.

L10 - Reactor pressurization line between the reactor pressurization line L8 and the air supply line L27.

L11 - Connecting line between the reactor pressurization line L8 and the pressure gauge line L12.

L12 - Pressure gauge line from the connecting line L11 to the gauge protector G1 and the air pressure gauge G2.

L13 - Reactor line between the reactor pressurization line L8 and the port R8 of the reactor R1.

L14 - Air line between the air supply line L27 and the valve V10.

L27 - Air supply line.

Valves involved

Operating valves/position

V3 - Valve in the air line L3/closed.

V4 - Valve in the water line L4/closed.

V5 - Valve in the vent line L5/closed.

V6 - Valve in the reaction gas line L6/closed.

V8 - Valve in the reactor pressurization line L8/open.

V10 - Valve between the air lines L14 and L1/open.

V13 - Outlet valve in the reactor R1/closed.

Check valves

V12 - Check valve in the sample line L17 prevents reaction gases from entering the sample circuit through the sample line.

Pressure regulation valves

AR1 - Pressure regulation valve in the air line L1.

AR3 - Pressure regulation valve in the air line L14.

AR5 - Pressure regulation valve having a precision of $\pm$ .02 psi in the reactor pressurization line L10.

Flow

Air

L27 through AR2 through L14 through V10 through L1 through AR1 into R11 to hold V13 closed.

L27 through AR5 through L10 through V8 through L8 through L13 through R8 into R1.

Reaction gas transfer mode (Gas to G.C.)

The ninth mode is the reaction gas transfer mode. The reaction gas is transferred to the gas chromatograph (G.C.). This requires enough

time to allow a representative sample to be received in the sample loop SL1 of the gas chromatograph.

Major components involved

R1 - Reactor

Lines involved

L1 - Air line between the valve V10 and the reactor outlet valve V13.

L2A - Line between the reaction gas line L6 and the gas chromatograph.

L6 - Reaction gas line between the reactor line L13 and the gas chromatograph line L2A.

L13 - Reactor line between the port R8 of the reactor R1 and the reaction gas line L6.

L14 - Air line between the air supply line L27 and the valve V10.

L27 - Air supply line.

Valves involved

Operating valves/position

V3 - Valve in the air line L3/closed.

V4 - Valve in the water line L4/closed.

V5 - Valve in the vent line L5/closed.

V6 - Valve in the reaction gas line L6/open.

V8 - Valve in the air pressure line L8/closed.

V10 - Valve between the air lines L14 and L1/open.

V13 - Outlet valve in the Reactor R1/closed.

Check valves

V12 - Check valve in the sample line L17 prevents reaction gas from entering the sample circuit through the sample line L17.

Pressure regulation valves

AR1 - Pressure regulation valve in the air line L1.

AR3 - Pressure regulation valve in the air line L14.

Flow

Air

L27 through AR3 through L14 through V10 through L1 through AR1 into R11 to hold V13 closed.

Reaction gas

R1 through R8 through L13 through V6 through L6 through L2A to gas chromatograph.

Time

40 seconds or as needed to ensure that the gas chromatograph has received a representative reaction gas sample.

Stop transfer mode (Stop)

The tenth mode is the stop transfer mode. The reaction gas valve V6 is closed. Time is allowed for the pressure in the gas chromatograph system to equalize.

Major components involved

R1 - Reactor

Lines involved

L1 - Air line between the valve V10 and the reactor outlet valve V13.

L14 - Air line between the air supply line L27 and the valve V10.

L27 - Air supply line.

Valves involved

Operating valves/position

V3 - Valve in the air line L3/closed.

V4 - Valve in the water line L4/closed.

V5 - Valve in the vent line L5/closed.

V6 - Valve in the reaction gas line L6/closed.

V8 - Valve in the air pressure line L8/closed.

V10 - Valve between the air lines L14 and L1/open.

V13 - Outlet valve in the Reactor R1/closed.

Check valves

V12 - Check valve in the sample line L17 prevents reaction gas from entering the sampling system through the sample line.

Pressure regulation valves

AR1 - Pressure regulation valve in air line L1.

AR3 - Pressure regulation valve in air line L14.

Flow

Air

L27 through AR3 through L14 through V10 through L1 through AR1 into R11 to hold V13 closed.

Time

5 seconds or as needed for the pressure in the gas chromatograph sample chamber to equilibrate.

Magnetic spin bar driver

The liquor within the reactor chamber R2 is stirred by the mixing rod R13 within the reactor and resting on the drain valve V13 in the bottom of the reactor. This rod is magnetically coupled with and rotated by the magnetic spin bar driver M2 in chamber M1.

The magnetic spin bar driver is shown in Figures 7 and 8. A powerful horseshoe magnet M3 faces upwardly toward the spin bar R13. The horseshoe magnet M3 is mounted on a rotating plate M4. Any type of mounting may be used. It may be adhered to the plate M4 with epoxy or other type of adhesive. It is shown mounted in an arcuate depression in the upper face of the plate M4.

The plate M4 rests on a base M5. Both the rotating plate M4 and the base M5 are shown as being circular in cross section. The base M5 has an upper flat horizontal supporting surface M6 around its periphery. A circular recessed section M7 is within the periphery. The recessed section M7 also has a flat horizontal surface below surface M6 and a vertical side wall that extends from its surface to the supporting surface M6. A circular further recessed section M8 is within section M7. The surface of recessed section M8 is also flat and below the surface of section M7. The section M8 also has a vertical side wall that extends from its surface to the surface of section M7. The periphery of the base M5, the periphery of the section M7 and the periphery of the section M8 are concentric.

The section M8 holds a nylon and glass ball bearing M9. The plate M4 has a cylindrical shaft M10 that fits and rotates within bearing M9. A motor section M11 of the plate M4 fits and rotates within the recessed section M7 of the base M5. There is a clearance between the motor section M11 and the surfaces of the recessed section M7. The motor section M11 is circular and concentric with both the cylindrical shaft M10 and the outer circular periphery M12 of the plate M5. The periphery M13 of the motor section M11 is broken by equally spaced radial slots or indentations M14.

An air line M15 extends through the base M5 below the recessed section M8. Two secondary air passages M16 extend from air line M15 angularly upwardly to the surface of the recessed section M7. The outlets of the secondary air passage M16 are aligned with the radial slots M14 to allow air to impinge against the side walls of the radial slots M14 and rotate the plate M4. The outlets of the secondary air passages M16 are shown as 180° apart and on opposite sides of air line M15. The outlets may be parallel to a tangent to the periphery of recessed section M7 or be angled toward the periphery. The outlets may be, as shown, near the periphery of recessed section M7.

Air from air line L7 passes through line M15 and passages M16 to impinge against the walls of the radial slots M14 to rotate the plate M4. The escaping air from the secondary air passages M16 also acts as a bearing for the plate M5 between the surface M17 of the plate M4 and the supporting surface M6 of the base M5. The air eventually escapes along the surface M6 and out through the gap between the base and the revolving plate.

The rotation of plate M4 rotates the magnet M3. The rotating magnet M3 rotates the spin bar R13.

The magnetic spin bar drive has the following components and operation:

<u>Major components involved</u>

M1 - Magnetic spin bar mixer chamber.

M2 - Magnetic spin bar mixer driver.

<u>Lines involved</u>

L7 - Air line from the air line L14 to the chamber M1.

L14 - Air line from the air supply line L27 to the air line L7.

L27 - Air supply line.

<u>Valves involved</u>

<u>Pressure regulation valves</u>

AR3 - Pressure regulation valve in the air line L14.

<u>Repair valves</u>

V7 - Repair valve in the air pressure line L7.

<u>Flow</u>

L27 through AR3 through L14 through V7 through L7 into M1 to operate M2.

It will be appreciated that the magnetic spin bar drive may also be turned off and on depending on whether the reactor chamber is filled or empty by changing the valve V7 to a solenoid operated on/off valve and operating it on the same cycle as valve V10 which controls the outlet valve V13 of the reactor. Valves V7 and V10 would open and close together.

Gas Chromatograph System

In the reactor the green liquor or white liquor is reacted with acid to form carbon dioxide and hydrogen sulfide gases. The concentration of these gases is measured in the gas chromatograph. The chromatograph outputs a continuous analog signal corresponding to the flow rate of gas through the detector of the chromatograph. By integrating this signal for the proper time intervals (corresponding to the time of appearance of carbon dioxide and hydrogen sulfide at the detector), the concentrations of carbon dioxide and hydrogen sulfide in the reaction gas are measured. Calibration of the reactor/gas chromatograph system using liquors of known concentration allows the carbon dioxide and hydrogen sulfide measurements to be converted directly to a determination of sodium carbonate and sodium sulfide in the liquor sample.

The analysis process takes about four minutes for both carbon dioxide and hydrogen sulfide. It may be necessary to analyze only for carbon dioxide in the green liquor and causticizer white liquor samples. This would reduce the analysis time for these samples to one and one-half minutes.

The gas chromatograph may be used to successively analyze the reaction gases from a number of reactors. For one slaking/causticizing line, three liquor samples should be analyzed, resulting in a three-reactor analyzer system. For this reason the valve V1 is a four position valve having four inlets from the reactors or other outside sources and one outlet to the gas chromatograph. It cycles through the four positions until is is at the proper position to receive reaction gas from the selected reactor. It requires approximately five seconds to move from one position to the next. Another five seconds is allowed to electronically check the position of the valve.

The inner details of a gas chromatograph will not be given. It is a standard piece of equipment and its details, other than allowing time for it to cycle through its procedure and the results of its analysis are not

important here. There are a number of valves in the gas chromatograph that allow the sample loop to be filled, the gas sample to be carried to the analysis column, and the sample loop and analysis column to be purged and backflushed. This discussion will not include the standard helium flush and backflush that occurs within the gas chromatograph itself since these are normal functions of the instrument. We will merely note that these valves and operations exist in any gas chromatograph and will give only a general overview of the process and the apparatus. The only procedures that will be described in detail are the external procedures.

The chromatrograph circuit has few parts. These are:

Components

Major components

- GC - Gas chromatograph/two positions: position one (standby) is used in three different modes - mode 1A (bypass); mode 1B (gas transfer); mode 1C (purge) - position two (analyze).
- SL1 - Sample loop for the gas chromatograph.

Lines

- L2 - Line to the gas chromatograph
  - L2A - Line from the reaction gas line L6 to the gas chromatograph GC.
  - L2B - Line from the calibration gas line L7 to the gas chromatograph line L2A.
  - L2C - Line from the air pressure line L10 to the gas chromatrograph line L2B.
- L6 - Reaction gas line from the reactor R1 to the gas chromatograph line L2A.
- L7 - Calibration gas line from the calibration gas supply to the gas chromatograph line L2B.
- L10 - Air pressure line from the air supply line L27 to the gas chromatograph line L2C.
- L14 - Air line from air supply line L27 to air line L53.
- L27 - Air supply line.
- L53 - Air line from air line L14 to valve V1 to operate the valve.

Valves

Operating valves

V1 - Valve in the gas chromatograph line L2A. Four positions to bring sample into gas chromatograph: position one (reactor one); position two (reactor two); position three (reactor three); position four (spare).

V2 - Valve in the high pressure air line L2C. Two positions: open; closed.

V6 - Valve in the reaction gas line L6. Two positions: open; closed.

V7 - Valve in the calibration gas line L7. Two positions: open; closed.

Pressure regulation valves

AR3 - Pressure regulation valve in air line L14.

AR5 - Pressure regulation valve in high pressure air line L10.

In the sequence of operations, the gas chromatograph takes a gas sample into the sample loop SL1, analyzes the gas sample, purges the sample from the system and backflushes the system. It then waits for a new sample to be supplied.

Standby mode (Standby)

The first mode is a standby mode. The gas chromatograph is waiting for a sample from the reactor circuit.

Major components involved

GC - Gas chromatograph/position one (standby)

Valves involved

Operating valves/position

V1 - Valve in gas chromatograph line L2A/position four (closed). This is exemplary. The valve may be in any position at start-up. It will depend upon the valve position when the system was shut down.

V2 - Valve in high pressure air line L2C/closed.

V6 - Valve in the reaction gas line L6/closed.

V7 - Valve in the calibration gas line L7/closed.

Flow

No flow of reaction gases.

Reposition mode (Reposition)

The second mode is a reposition mode (Reposition). The valve V1 is repositioned around its four positions until it is lined up with the right reactor. It moves in the same direction, either clockwise or counter-clockwise, requiring five seconds to move. An additional five seconds is alloted for the system to check the position of the valve. If its location is not right, it will move again and be checked again. This will continue until it is in the right position. The other valves and the gas chromatograph remain as they are.

Standby mode (Standby 2)

The third mode is a new Standby mode (Standby 2) in which all the valves remain in their positions until the reactor circuit is ready to transfer a gas sample.

Reaction gas transfer mode (Gas to G.C.)

The fourth mode is a reaction gas transfer mode. The gas chromatograph is internally valved so that the reaction gas goes through the sample loop and then to the vent to sewer. The time of this transfer is long enough for a representative sample to be received. The initial gas entering the sample loop SL1 will usually not be representative of the bulk of gas in the reactor. The lines from the reactor to the gas chromatograph are initially filled with air from the previous air purge mode. Air must be flushed from these lines and the sample loop to ensure a representative sample of reaction gas is obtained. It requires a period of time to obtain a steady state sample in the sample loop. Consequently the time will vary depending on the several factors influencing the gas transfer to the sample loop. These factors may include the arrangement and dimensions of the tubing between the reactor and the sample loop, the sample purge conditions, and the conditions of pressure, gas composition, etc. existing in the reactor itself at the time of gas transfer. The time is usually between 40 and 60 seconds.

Major components involved

GC - Gas chromatograph/mode 1A (gas transfer).

SL1 - Sample loop for the gas chromatograph.

Lines involved

L2A - Gas chromatograph line from the reaction gas line L6 to the sample loop SL1.

L6 - Reaction gas line from the reactor to the line L2A.

L13 - Reactor line from the port R8 of the reactor R1 to the line L6.

Valves involved

Operating valves/position

V1 - Valve in gas chromatograph line L2A/position one (reactor circuit one).

V2 - Valve in high pressure air line L2C/closed.

V6 - Valve in reaction gas line L6/open.

V7 - Valve in the calibration gas line L7/closed.

Flow

Reacton gas

R1 through R6 through L13 through V6 through L6 through L2A through V1 through SL1 to sewer.

Time

40 seconds or as needed to obtain a representative sample of reaction gas in the sample loop. The time of 40 seconds is representative. The length of time is the time required to obtain a representative sample of reaction gas in the sample loop SL1.

Stop sample mode (Stop)

The fifth mode is a stop sampling mode in which the reaction gas to the gas chromatograph is stopped and the gas pressure in the sample loop is allowed to equalize with atmospheric pressure.

Major components involved

GC - Gas chromatograph/mode 1B (gas transfer).

SL1 - Sample loop of the gas chromatograph.

Valves involved

Operating valves/position

V1 - Valve in gas chromatograph line L2A/position one (reactor circuit one).

V2 - Valve in high pressure air line L2A/closed.

V6 - Valve in reaction gas line L6/closed.

V7 - Valve in calibration gas line L7/closed.

Flow

No flow

Time

5 seconds or as needed for conditions in sample loop to equilibrate.

Analysis mode (Analyze)

The sixth mode is an analysis mode in which the sample is analyzed in the gas chromatograph. There is no change in the external circuit. The change is in the internal system of the gas chromatograph. It switches from position two (gas transfer) to position three (analyze).

Major components involved

GC - Gas chromatograph/position two (analyze).

SL1 - Sample loop of the gas chromatograph.

Valves involved

Operating valves/position

V1 - Valve in gas chromatograph line L2A/position one (reactor circuit one).

V2 - Valve in high pressure air line L2A/closed.

V6 - Valve in the reaction gas line L6/closed.

V7 - Valve in the calibration gas line L7/closed.

Flow

Helium through sample loop carries reactor gas through column past detector out vent.

Time

4 minutes depending on elutriation time of carbon dioxide and hydrogen sulfide through column. The time may be more or less than 4 minutes depending on the length of the column, column packing characteristics, helium flow rate, etc. The time will be one and one-half minutes if the analysis is only of carbon dioxide. Again, the time may be more or less than one and one-half minutes because of other factors.

Sample purge mode (Purge)

The seventh mode is a gas purge mode in which high pressure air is used to purge the sample from the sample loop and the lines between the sample loop and reactor.

Major components involved

GC - Gas chromatograph/mode 1C (purge).

SL1 - Sample loop for gas chromatograph.

Lines involved

L2 - Gas chromatograph line from high pressure air line L10 to the sample loop SL1. Includes lines L2A, L2B and L2C.

L10 - High pressure line between air supply line L27 and the gas chromatograph line L2.

L27 - Air supply line.

Valves involved

Operating valves/position

V1 - Valve in the gas chromatograph line L2A/position one (reactor circuit one).

V2 - Valve in the high pressure air line L2C/open.

V6 - Valve in the reaction gas line L6/closed.

V7 - Valve in the calibration gas line L7/closed.

Pressure regulation valves

AR5 - Pressure regulation valve in the high pressure air line L10.

Flow

Air

L27 through AR5 through L10 through V2 through L2 through SL1 to vent to sewer.

Time

1 minute 5 seconds or as needed to adequately purge lines and loop.

During the time that the liquor sample in reactor 1 is completing its reaction, the valve V1 would move to postions 2 and 3, and the gas chromatograph would be analyzing the gas samples from the second and third reactors.

Data collection and analysis

The gas chromatograph output circuitry generates voltage "peaks" which correspond to the appearance of each gas component at the detector of the gas chromatograph. The time interval (from the start of the analysis) during which each component (air, carbon dioxide and hydrogen sulfide) will

pass through the detector is a characteristic of each component gas. This time interval during which each component appears at the detector is very reproducible and is easily established for each gas. The gas chromatograph output circuitry generates a continuous 0-1 volt analog signal which is proportional to the flow of gas through the detector. During the time interval each component passes through the detector, a voltage "peak" is generated in response to the appearance of the component. Figure 9 is a plot of G.C. voltage output over the course of a gas analysis resulting from a typical green liquor sample. Each component of the gas sample is identified, and the time interval during which it appears is noted. The voltage "peaks" for each component are easily observed from the figure. The integrated voltage for each component (which is equal to the area under each peak) is proportional to the amount of the component in the gas sample. Furthermore, the carbon dioxide and hydrogen sulfide integrated voltages are proportional to the sodium carbonate and sodium sulfide concentrations in the liquor. The integrated peak areas for CO_2 and H_2S are therefore a measure of the Na_2CO_3 and Na_2S concentrations in the liquor sample.

The data collection circuit enables the carbonate/sulfide analyzer to convert the voltage peaks generated by the gas chromatograph into values which correspond to the concentrations of Na_2CO_3 and Na_2S in the liquor. The data collection circuit consists of the following major components:

GC - Gas chromatograph output circuitry
VCO - Voltage-to-frequency converter
M - Microcomputer

A schematic of the data collection circuit is shown in Figure 10. The associated wiring and components needed to link the major components are known and are therefore not illustrated.

In order to calculate the concentration of Na_2CO_3 and Na_2S in the liquor sample, the CO_2 and H_2S voltage peaks must be integrated. There are many methods which may be utilized to accomplish the integration. The preferred method of peak integration is to utilize a voltage-to-frequency converter (VCO) to convert the 0-1 volt G.C. output signal to a 0-10,000 HZ frequency signal. The continuous series of electronic pulses thus generated is utilized as input to a digital microcomputer. The time

intervals corresponding to the appearance of the CO_2 and H_2S peaks are programmed into the microcomputer software. During the discrete time intervals corresponding to the peak for each component, the microcomputer counts the total number of pulses generated by the VCO for the peak period. The number of pulses thus counted is a measure of the peak area. The peak area measurements thus obtained for CO_2 and H_2S are proportional to the concentrations of Na_2CO_3 and Na_2S, respectively, in the liquor sample.

The microcomputer, furthermore, allows for calibration of the analyzer by providing the ability to convert the pulse count measurements to direct determinations of Na_2CO_3 and Na_2S in the liquor. The pulse count is directly proportional to the concentration of chemical in the liquor. By analyzing several liquors of known concentrations, and measuring the pulse counts generated from these known liquors, one can easily establish the correct conversion factors to convert the pulse counts to concentration measurements. These conversion factors are then stored in the microcomputer software. The conversion factors are applied to the pulse counts for all subsequent liquor samples to provide direct determinations of Na_2CO_3 and Na_2S in the liquor. The liquor concentrations may be given as printed data or converted to analog signals for use as input to control devices. Methods of generating such outputs are varied and are well known.

<u>Reactor temperature measurement system</u>

The measurement of sodium carbonate and sodium sulfide generated by the carbonate/sulfide analyzer have been observed to be affected by the temperature at which the reaction occurs. The reaction temperature is primarily governed by the temperature inside the analyzer cabinet. The measurements generated by the analyzer vary in direct proportion with the cabinet temperature. As the cabinet temperature increases, the resultant measurements of sodium carbonate and sodium sulfide correspondingly increase. There must be compensation for this phenomena if accurate measurements are to be obtained for all samples despite reactor temperature variations.

It has been determined that the best method of eliminating measurement errors due to reactor temperature variations is to apply a correction factor to each measurement based on the cabinet termperature during the reaction. In order to determine the proper factor for each measurement, the cabinet temperature is measured at the completion of

each reaction. The proper correction factors, based on the cabinet temperature, are then automatically computed for each sample and applied to the "raw" or "uncorrected" values generated by the gas chromatograph. This strategy has been found to be an effective method of eliminating errors caused by reaction temperature variations.

It has been found that for each $1^{o}C$ deviation from a reference temperature the G.C. measured area for Na_2CO_3 increases or decreases 0.4% and the G.C. measured area for Na_2S increases or decreases 0.7%. The correction for Na_2CO_3 is:

$$CA = MA\ [1 + 0.004\ (To - T)]$$

and for Na_2S is:

$$CA = MA\ [1 + 0.007\ (To - T)]$$

CA = corrected area

MA = G.C. measured area

To = reference temperature

T = actual temperature of gas from reactor

As an example if the reference temperature is $30^{o}C$ and the actual temperature is $27^{o}C$, then for Na_2CO_3

$$CA = MA\ [1 + 0.004\ (30 - 27)] = 0.988\ MA$$

and for Na_2S

$$CA = MA\ [1 + 0.007\ (30 - 27)] = 0.979\ MA$$

The temperature measurement system uses a resistance temperature detector (RTD) mounted inside the cabinet, and a relay which closes to allow the detector to be sampled by the analyzer data collection system. The relay closes to allow sampling of the detector immediately upon completion of the transfer of reactor gases to the gas chromatograph sample chamber. It remains closed for 20 seconds or as needed to obtain an accurate temperature measurement. The RTD signal is converted to a temperature measurement in the data collection software.

A resistance temperature detector has been found to be the best suited temperature measuring device. The detector element exhibits an electrical resistance which varies directly with temperature. This resistance is easily measured electronically and is easily converted to a temperature reading since the calibration of these elements is well documented. Other devices, such as thermocouples or thermistors, which exhibit electrical properties that vary as a function of temperature could also be utilized in this application.

Materials of construction

All materials have been selected to ensure maximum serviceability and resistance to the effects of heat, pressure, and the corrosive properties of the liquid and gas streams. We have found the following materials to be the best for the specific applications listed below:

The reactor's top and base is constructed of P.V.C. (polyvinyl chloride). The fixture at top of pump is P.V.C. The mounting board for all solenoids, etc. is P.V.C. The magnetic spin bar driver is P.V.C.

The reactor cylinder and the acid pump cylinder are glass.

All tubing that is in direct contact with acid or the gases is teflon, all other tubing is nylon. All fittings that are in direct contact with acid or the gases are nylon. The reactor gas to gas chromatograph and the vent solenoids are teflon. All check valves are teflon. The sample loop is nylon.

The acid pump piston is teflon coated 316 S.S. (stainless steel). The fittings that come into indirect contact with gases or those that are flushed with air or water are 316 S.S. All fittings, tubing, valves, columns, etc. within the gas chromatograph are 316 S.S. The gas isolation valve mounted on front of gas chromatograph is 316 S.S. The air, water, pressurization and purge solenoids are 304 S.S.

All fittings on the air and water lines that are on inlet sides of solenoid or regulators are brass. All regulators are aluminum. The liquor/acid sample valve is Hastalloy C.

Operation

In an overall system these circuits would operate together. The precise operation will depend upon the mill configuration. A typical operation for one reactor circuit is shown in the following table. In this table, the operating valves, the valve positions - open (O), closed (C) or position (1, 2) -, the change of position (*), and the time are given. For an analyzer utilizing multiple reactor circuits, the time of start-up of each circuit would be offset so as to result in no overlap of gas chromatograph operation. Otherwise the logic and sequencing for each circuit will in general be identical, although minor modifications could be made to each individual reactor circuit in response to differences in liquor strength or other characteristics without adversely affecting the overall system operation.

Table I

Time	Filter	Sample	Reactor	Gas Chrom.
00:00				
	Bypass	Standby 1	Standby	Standby
	V21 C	V11 1S	V3 C	V1 4
	V22 C	V14 1S	V4 C	V2 C
	V24 O	V17 1F	V5 C	V6 C
	V26 C	AP2 1F	V6 C	V7 C
	V28 1B	(00:05)	V8 C	GC 1
	V29 C		V10 O	(20:35)
	(00:40)		V13 C	
00:05		00:05	00:05	
		Reposition 1	Vent	
		V11 2T *	V3 C	
		V14 2T *	V4 C	
		V17 1F	V5 O *	
		AP2 1F	V6 C	
00:10		00:05	V8 C	
		Transfer	V10 O	
		V11 2T	V13 C	
		V14 2T	(00:35)	
		V17 2T *		
		AP2 2T *		
00:40	00:40	00:30	00:35	
	Filter	Reposition 2	Standby	
	V21 O *	V11 1S *	V3 C	
	V22 C	V14 1S *	V4 C	
	V24 C *	V17 1F *	V5 C *	
	V26 C	AP2 1F *	V6 C	
00:45	V28 2F *	00:05	V8 C	
	V29 C	Standby 2	V10 O	
	(01:00)	V11 1S	V13 C	
		V14 1S	(02:15)	
		V17 1F		
		AP2 1F		
01:40	01:00	00:55		
	Sample	Sample		
	V21 O	V11 1S		
	V22 O *	V14 1S		
	V24 C	V17 1F		
	V26 C	AP2 1F		
	V28 2F	(01:00)		
	V29 C			
02:40	01:00	01:00		
	Stop	Standby 3		
	V21 O	V11 1S		
	V22 C *	V14 1S		
	V24 C	V17 1F		
	V26 C	AP2 1F		
	V28 2F	(01:55)		
	V29 C			

Time	Filter	Sample	Reactor	Gas Chrom.
02:45	00:05			
	Backflush 1			
	V21 C *			
	V22 C			
	V24 C			
	V26 C			
	V28 2F			
	V29 C			
02:55	00:10		02:15	
	Backflush 2		Drain	
	V21 C		V3 O *	
	V22 C		V4 C	
	V24 O *		V5 C	
	V26 O *		V6 C	
	V28 1B *		V8 C	
	V29 C		V10 C *	
	(00:15)		V13 O *	
03:05			00:10	
			Fill	
03:10	00:15		V3 C *	
	Bypass		V4 O *	
	V21 C		V5 O *	
	V22 C		V6 C	
	V24 O		V8 C	
	V26 C *		V10 O *	
	V28 1B		V13 C *	
03:25	V29 C		00:20	
	(13:00)		Drain	
			V3 O *	
			V4 C *	
			V5 C *	
			V6 C	
			V8 C	
			V10 C *	
			V13 O *	
03:35			00:10	
			Fill	
			V3 C *	
			V4 O *	
			V5 O *	
			V6 C	
			V8 C	
			V10 O *	
			V13 C *	
03:55			00:20	
			Drain	
			V3 O *	
			V4 C *	
			V5 C *	
			V6 C	
			V8 C	
			V10 C *	
			V13 O *	

Time	Filter	Sample	Reactor	Gas Chrom.
04:05			00:10	
			Fill	
			V3 C *	
			V4 O *	
			V5 O *	
			V6 C	
			V8 C	
			V10 O *	
			V13 C *	
04:25			00:20	
			Drain	
			V3 O *	
			V4 C *	
			V5 C *	
			V6 C	
			V8 C	
			V10 C *	
			V13 O *	
04:35		01:55	00:10	
		Reposition 3	Vent	
		V11 2T *	V3 C *	
		V14 2T *	V4 C	
		V17 1F	V5 O *	
		AP2 1F	V6 C	
		(00:05)	V8 C	
			V10 O *	
			V13 C *	
04:40		00:05	00:05	
		Transfer	Transfer	
		V11 2T	V3 C	
		V14 2T	V4 C	
		V17 2T *	V5 C *	
		AP2 2T *	V6 C	
		(00:30)	V8 C	
			V10 O	
			V13 C	
05:10		00:30	00:30	
		Reposition 4	Reaction 1	
		V11 1S *	V3 C	
		V14 1S *	V4 C	
		V17 1F *	V5 C	
		AP2 1F *	V6 C	
05:15		00:05	V8 C	
		Standby 2	V10 O	
		V11 1S	V13 C	
16:10		V14 1S	11:00	
	Filter	V17 1F	Pressure	
	V21 O *	AP2 1F	V3 C	
	V22 C	(11:55)	V4 C	
	V24 C *		V5 C	
	V26 C		V6 C	
	V28 2F *		V8 O *	
	V29 C		V10 O	
	(01:00)		V13 C	

Time	Filter	Sample	Reactor	Gas Chrom.
16:20			00:10 Reaction 2 V3 C V4 C V5 C V6 C V8 C * V10 O V13 C (04:25)	
17:10	01:00 Sample V21 O V22 O * V24 C V26 C V28 2F V29 C	11:55 Sample V11 1S V14 1S V17 1F AP2 1F (01:00)		
18:10	01:00 Stop V21 O V22 C * V24 C V26 C V28 2F V29 C	01:00 Standby 3 V11 1S V14 1S V16 1F AP2 1F (05:10)		
18:15	00:05 Backflush 1 V21 C * V22 C V24 C V26 C V28 2F V29 C			
18:25	00:10 Backflush 2 V21 C V22 C V24 O * V26 O * V28 1B * V29 C			
18:40	00:15 Bypass V21 C V22 C V24 O V26 C * V28 1B V29 C (16:15)			
20:35				20:35 Reposition V1 1 * V2 C V6 C V7 C GC 1
20:40				00:05 Standby V1 1 V2 C V6 C V7 C GC 1

Time	Filter	Sample	Reactor	Gas Chrom.
20:45			04:25	00:05
			Gas to G.C.	Gas to G.C.
			V3 C	V1 1
			V4 C	V2 C
			V5 C	V6 O *
			V6 O *	V7 C
			V8 C	GC 1
			V10 O	(00:40)
			V13 C	
21:25			00:40	00:40
			Stop	Stop
			V3 C	V1 1
			V4 C	V2 C
			V5 C	V6 C *
			V6 C *	V7 C
			V8 C	GC 1
			V10 O	(00:05)
			V13 C	
21:30			00:05	00:05
			Drain	Analyze
			V3 O *	V1 1
			V4 C	V2 C
			V5 C	V6 C
			V6 C	V7 C
			V8 C	GC 2
			V10 C *	(04:00)
			V13 O *	
21:40			00:10	
			Fill	
			V3 C *	
			V4 O *	
			V5 O *	
			V6 C	
			V8 C	
			V10 O *	
			V13 C *	
22:00			00:20	
			Drain	
			V3 O *	
			V4 C *	
			V5 C *	
			V6 C	
			V8 C	
			V10 C *	
			V13 O *	

Time	Filter	Sample	Reactor	Gas Chrom.
22:10			00:10	
			Fill	
			V3 C *	
			V4 O *	
			V5 O *	
			V6 C	
			V8 C	
			V10 O *	
			V13 C *	
22:30			00:20	
			Drain	
			V3 O *	
			V4 C *	
			V5 C *	
			V6 C	
			V8 C	
			V10 C *	
			V13 O *	
22:40			00:10	
			Fill	
			V3 C *	
			V4 O *	
			V5 O *	
			V6 C	
			V8 C	
			V10 O *	
			V13 C *	
23:00			00:20	
			Drain	
			V3 O *	
			V4 C *	
			V5 C *	
			V6 C	
			V8 C	
			V10 C *	
			V13 O *	
23:10		05:10	00:10	
		Reposition 3	Vent	
		V11 2T *	V3 C *	
		V14 2T *	V4 C	
		V17 1F	V5 O *	
		AP2 1F	V6 C	
		(00:05)	V8 C	
			V10 O *	
			V13 C *	

Time	Filter	Sample	Reactor	Gas Chrom.
23:15		00:05 Transfer V11 2T V14 2T V17 2T * AP2 2T * (00:30)	00:05 Transfer V3 C V4 C V5 C * V6 C V8 C V10 O V13 C	
23:45		00:30 Reposition 4 V11 1S * V14 1S * V17 1F * AP2 1F *	00:30 Reaction 1 V3 C V4 C V5 C V6 C V8 C V10 O V13 C (11:00)	
23:50		00:05 Standby 2 V11 1S V14 1S V17 1F AP2 1F (11:55)		
25:30				04:00 Purge V1 1 V2 O * V6 C V7 C GC 1 *
26:35				01:05 Standby V2 C *
34:45	16:15 Filter		11:00 Pressure	
	Continues	Continues	Continues	Continues

Use

Figures 11, 12 and 13 are schematic diagrams showing the use of the apparatus in the causticizing system.

Control loop 1 seen in Figure 11 discloses the use of the analyzer in controlling the sodium carbonate concentration in the green liquor to the slaker. In this diagram green liquor from the green liquor clarifier GLC flows through the mill liquor line ML1 and is pumped by the green liquor pump GLP to the slaker S. Lime is added to the green liquor at the slaker S. There is an additional line in this diagram. That is line L40 which carries a portion of the weak wash into the mill liquor line ML1.

The line L28/29 designates two lines, L29 which carries the liquor from the mill liquor line ML1 to the reactor system RS1 and L28 which returns the liquor from the reactor system RS1 to the mill liquor line ML1. Each of the reactor systems - RS1, RS2 and RS3 - includes a filter

circuit, a sample circuit and a reactor circuit. These circuits are shown in Figures 1-3. The line L2 carries the reaction gas from the reactor system RS1 to the gas chromatograph/analyzer GC/A in which the gas is analyzed for carbon dioxide (resulting from sodium carbonate in the liquor) and hydrogen sulfide (resulting from sodium sulfide) as described above. The analyzer, using the carbon dioxide analysis, outputs a signal through the control line CL1 to the controller which operates the valve V40 to increase or decrease the amount of weak wash flowing through line L40 into ML1 in order to maintain a constant sodium carbonate concentration in the green liquor going to the slaker.

The hydrogen sulfide analysis has several uses. It is an indication of the reduction efficiency in the recovery boiler. The sodium sulfide concentration can be given to the recovery boiler operator to confirm to him that the reduction efficiency is good or to allow him to make corrections to improve the reduction efficiency. It is also an indication of the potential efficiency in the causticizing operation. As the concentration of sodium carbonate or sodium sulfide in the green liquor increases, the efficiency of the causticizing operation decreases. This will give the operator information about the causticizing reaction that the green liquor is about to undergo and allow the causticizing operator to take corrective action.

The second control loop of this system is shown in Figure 12. This loop controls the balance of green liquor and lime, and in fact controls the entire slaking operation. A "clear" liquor sample is taken from the calcium carbonate mud separator at either the slaker or first causticizer. This "clear" liquid is then filtered to remove all the remaining calcium carbonate mud. The sodium ~~carbonate and sodium sulfide concentration~~ in this filtered liquor is then measured in the GC/A from the reaction gas from the second reactor system, RS2.

The control loop logic will contain a set point for the desired sodium carbonate concentration in the liquor. This set point Na_2CO_3 concentration will, as proven by mill experience, result in the best combination of high conversion efficiency of Na_2CO_3 to NaOH, low Na_2CO_3 "deadload," and acceptable mud settling characteristics. The loop will then control the slaker operation via mass flow of sodium carbonate to the slaker so as to maintain and control this concentration of Na_2CO_3 in the liquor

leaving the slaker. There are two ways of controlling the sodium carbonate concentration in the slaker or first causticizer. One is the usual method of controlling the amount of lime being added to the slaker. The other, and the method the inventors consider to be significantly better, is shown in Figure 12. In this method the amount of sodium carbonate in the green liquor is controlled by loop 1 as is described above. The amount of this green liquor added to the slaker is controlled by loop 2. The amount of sodium carbonate and sodium sulfide in the white liquor from the first causticizer or slaker is determined by the GC/A from the reaction gases from RS2. A signal, based on the sodium carbonate, is then sent through control line CL2 to the controller which operates the valve V41 to increase or decrease the amount of green liquor flowing through ML1 into the slaker S.

The measurement of the chemical concentrations in the white liquor is taken from the line between the clear white liquor storage tank and the digester or digesters. The concentrations of sodium sulfide and sodium carbonate in the white liquor are determined directly by analysis by the GC/A of the reaction gases from the third reaction system, RS3. The amount of sodium hydroxide in the white liquor, however, must be determined indirectly. There are three pieces of information which must be combined to yield the sodium hydroxide concentration in the white liquor.

1. The sodium carbonate concentration in the white liquor;
2. The sodium carbonate concentration in the green liquor;
3. The sodium hydroxide concentration in the green liquor.

Measurements 1 and 2 are used to determine the amount of carbonate in the green liquor which, in the slaking/causticizing operation, has been converted to sodium hydroxide in the white liquor. The difference between the amount of Na_2CO_3 entering the system with the green liquor and the amount of Na_2CO_3 leaving with the white liquor is the concentration of NaOH which has been produced in the white liquor due to the causticizing reaction. All chemical concentrations are expressed on a sodium oxide (Na_2O) basis. Some sodium hydroxide also enters the system with the green liquor. This sodium hydroxide passes unchanged through the system to the white liquor and must be accounted for. This source of NaOH in the system is relatively stable - a periodic (every eight hour) determination of NaOH in the green liquor may be manually performed by an operator and entered into the analyzer software.

The determination of the NaOH in the green liquor may be performed directly in titration of a green liquor sample. It may alternatively be determined indirectly by titrating the NaOH in the white liquor. The amount of NaOH in the white liquor which cannot be accounted for by the amount of NaOH generated in recausticizing is the amount of NaOH which has entered with the green liquor. It is recommended that the NaOH in the green liquor be determined by the indirect method, which has the advantage of reducing errors caused by time lags in the process. The amount of NaOH associated with the green liquor is then stored in the microprocessor memory until updated by another titration. This value is used to update each subsequent white liquor sodium hydroxide determination.

The analyzer will solve the following equation for each succeeding sample to determine the sodium hydroxide concentration in the white liquor:

$$\text{NaOH (white liquor)} = Na_2CO_3 \text{ (green liquor)} - Na_2CO_3 \text{ (white liquor)} + \text{NaOH (green liquor)}$$

The carbonate analysis is updated with each sample every 19 minutes. The determination of sodium hydroxide in the green liquor is updated by manual titration of a green or white liquor sample when necessary, usually every eight hours. An updated, complete clarified white liquor analysis (determination of sodium hydroxide, sodium sulfide, and sodium carbonate) is provided to the digester operator or digester process computer every 12 to 19 minutes.

The system software must also take into consideration the time delays in the slaking, causticizing and clarification operations in order to correctly determine the current NaOH concentration in the white liquor. This will determine the amount of chemicals to be added to the digester in order to control the pulping process.

Cascaded Control Opportunities

In many applications it will be sufficient and desirable to utilize carbonate/sulfide analyzer measurements as the primary input to process control devices. However, in some applications it may be advantageous to control the process directly with a measurement device providing a more immediate but less accurate (in terms of sodium carbonate concentration) response to process changes. If these devices are utilized, measurements

from the carbonate/sulfide analyzer should be used as set point control signals for the primary controllers. This "cascaded" type control system will greatly improve the accuracy of the primary control measurement devices and improve control of the process.

Several measurement devices such as conductivity probes, density gauges, etc. provide rapid response to process changes. However, these devices provide only indirect measurements of the sodium carbonate concentration - they respond to the concentration of all chemicals in the process stream. The ratio of sodium carbonate to total chemicals in the process stream will vary with time, resulting in improper determinations of sodium carbonate concentration and less precise control of the process than could be obtained if sodium carbonate was measured directly. However, the changes which influence the calibration of these devices in measuring sodium carbonate concentration occur slowly - certainly greater than the 15-20 minute sampling period generated by the carbonate/sulfide analyzer.

The direct measurements of sodium carbonate generated by the carbonate/sulfide analyzer may be used as a set point control input to each primary control device. This practice will have the effect of adjusting the calibration of the primary device (conductivity probe, density gauge, etc.) every 15-20 minutes so that it is an accurate indicator of Na_2CO_3 concentration despite the previously mentioned variations in the ratio of Na_2CO_3/total chemicals. A cascaded control strategy of this type will have the advantage of having both an accurate method of determining sodium carbonate concentrations in the process and the ability to respond immediately to changes in the process.

This is illustrated in Figure 14. The main items are the dissolving tank DT, the green liquor clarifier GLC, the green liquor pump GLP, the slaker S and the first causticizer C1. Mill liquor line ML1 carries green liquor from dissolving tank DT to the green liquor clarifier GLC, and mill liquor line ML2 carries green liquor from the green liquor clarifier GLC to the slaker S. The principal weak wash line L42 carries weak wash to lines L40 and L41.

The weak wash in line L41 is used to dissolve the smelt in the dissolving tank DT. The amount of weak wash going to the dissolving tank DT through line L41 is controlled by valve V41. The amount of weak wash is determined by the density of the green liquor from the dissolving tank DT.

This is monitored in mill line ML1 by the density meter DM1. The signal from the density meter DM1 is carried through control line CL1 to the valve controller CN1. The valve V41 is controlled by CN1 with a signal which passes through control line CL2. This is a standard local control loop in which a local direct measurement is used to monitor the process conditions.

Figure 14 also illustrates the use of local conditions to monitor and control the amount of weak wash entering ML2 to maintain the carbonate level in the green liquor. However, in this instance the gas chromatograph/analyzer is used to determine the set points for this local control.

The valve V40 is used to control the flow of weak wash in line L40, which is the amount of weak wash which will enter the mill liquor line ML2. This is monitored locally be a density meter DM2 which sends a signal through control line CL3 to the control unit CN2. CN2 operates the control valve V40 to increase or decrease the flow of weak wash to maintain the density in ML2 at a specified level. However, the density of the liquor is not a direct indication of sodium carbonate in the liquor. A sample of the density-controlled liquor from ML2 is taken and analyzed for sodium carbonate concentration by reactor system RS1 and the gas chromatograph/analyzer unit GC/A. This direct determination of sodium carbonate is utilized to send a set point signal through control line CLS to CN2 in order to adjust the density set point so that the density more accurately reflects the sodium carbonate concentration in the liquor.

CLAIMS

1. A process comprising
clarifying pulp mill green liquor,
transporting said clarified green liquor to a slaker,
adding weak wash to said clarified green liquor while said clarified green liquor is being transported to said slaker,
mixing said weak wash with said clarified green liquor before said slaker to provide a green liquor of controlled sodium carbonate concentration,
determining the concentration of sodium carbonate in said controlled green liquor after said mixing and before said slaker, and
adjusting the volume of said weak wash being added to said clarified green liquor in response to changes in the concentration of sodium carbonate in said controlled green liquor to maintain the concentration of sodium carbonate in said controlled green liquor substantially constant,
adding lime to said controlled green liquor in said slaker to react sodium carbonate in said green liquor with calcium hydroxide generated from said lime to form a reaction mixture of green liquor, lime and their reaction products,
transporting said reaction mixture from said slaker,
determining the concentration of sodium carbonate in said reaction mixture,
adjusting the flow of controlled green liquor into said slaker in response to a change in sodium carbonate concentration in said reaction mixture.

2. The process of claim 1 in which
each of said steps of determining the concentration of sodium carbonate comprises
taking a sample from the appropriate liquor stream, and
determining the concentration of sodium carbonate in said sample.

3. The process of claim 2 further comprising
removing the suspended solids from each said sample prior to making said determination of sodium carbonate concentration.

4. The process of claim 1 further comprising

transporting said reaction mixture through a plurality of serially connected causticizing vessels to allow the reaction to continue.

5. The process of claim 4 in which

each of said steps of determining the concentration of sodium carbonate comprises

taking a sample from the appropriate liquor stream, and

determining the concentration of sodium carbonate in said sample.

6. The process of claim 5 further comprising

removing suspended solids from each said sample prior to making said determination of sodium carbonate concentration.

7. A process comprising

burning pulp mill digestion spent liquors in a furnace to generate an inorganic smelt,

dissolving said smelt to generate a pulp mill green liquor comprising sodium carbonate, sodium sulfide, soluble impurities and insoluble impurities,

clarifying said pulp mill green liquor to remove said insoluble impurities,

transporting said clarified green liquor to a slaker,

adding lime to said green liquor in said slaker to react sodium carbonate in said green liquor with calcium hydroxide generated from said lime to form a reaction mixture of green liquor, lime and their reaction products,

transporting said reaction mixture from said slaker through a plurality of serially connected causticizing vessels to allow said reaction to continue,

thereafter separating said reaction mixture into a clarified white liquor and a calcium carbonate mud,

returning said clarified white liquor to said pulp digestion process,

transporting said calcium carbonate mud to a washing tank,

washing said calcium carbonate mud with water to form a weak wash liquor,

using part of said weak wash liquor to dissolve said smelt,

adding a part of said weak wash liquor to said clarified green liquor while said clarified green liquor is being transported to said slaker,

mixing said weak wash liquor and said clarified green liquor before said slaker to provide a green liquor of controlled sodium carbonate concentration,

determining the concentration of sodium carbonate in said controlled green liquor after said mixing and before said slaker,

adjusting the volume of said weak wash liquor being added to said clarified green liquor in response to changes in the concentration of sodium carbonate in said controlled green liquor to maintain the concentration of sodium carbonate in said controlled green liquor substantially constant,

determining the concentration of sodium carbonate in the reaction mixture,

adjusting the flow of controlled green liquor into said slaker in response to changes in sodium carbonate concentration in said reaction mixture.

8. The process of claim 7 in which

each of said steps of determining the concentration of sodium carbonate comprises

taking a sample from the appropriate liquor stream, and

determining the concentration of sodium carbonate in said sample.

9. The process of claim 8 further comprising

removing the suspended solids from each said sample prior to making said determination of sodium carbonate concentration.

10. A process comprising

clarifying pulp mill green liquor,

transporting said clarified green liquor to a slaker,

adding water to said clarified green liquor while said clarified green liquor is being transported to said slaker,

mixing said water with said clarified green liquor before said slaker to provide a green liquor of controlled sodium carbonate concentration,

determining the concentration of sodium carbonate in said controlled green liquor after said mixing and before said slaker, and

adjusting the volume of said water being added to said clarified green liquor in response to changes in the concentration of sodium carbonate

in said controlled green liquor to maintain the concentration of sodium carbonate in said controlled green liquor substantially constant,

adding lime to said controlled green liquor in said slaker to react sodium carbonate in said green liquor with calcium hydroxide generated from said lime to form a reaction mixture of green liquor, lime and their reaction products,

transporting said reaction mixture from said slaker,

determining the concentration of sodium carbonate in said reaction mixture,

adjusting the flow of controlled green liquor into said slaker in response to a change in sodium carbonate concentration in said reaction mixture.

11. The process of claim 10 in which

each of said steps of determining the concentration of sodium carbonate comprises

taking a sample from the appropriate liquor stream, and

determining the concentration of sodium carbonate in said sample.

12. The process of claim 11 further comprising

removing the suspended solids from each said sample prior to making said determination of sodium carbonate concentration.

13. The process of claim 10 further comprising

transporting said reaction mixture through a plurality of serially connected causticizing vessels to allow the reaction to continue.

14. The process of claim 13 in which

each of said steps of determining the concentration of sodium carbonate comprises

taking a sample from the appropriate liquor stream, and

determining the concentration of sodium carbonate in said sample.

15. The process of claim 14 further comprising

removing suspended solids from each said sample prior to making said determination of sodium carbonate concentration.

16. A process comprising

clarifying pulp mill green liquor,

transporting said clarified green liquor to a slaker,

adding lime to said green liquor in said slaker to react sodium carbonate in said green liquor with calcium hydroxide generated from said lime to form a reaction mixture of green liquor, lime and their reaction products,

transporting said reaction mixture from said slaker,

determining the concentration of sodium carbonate in said reaction mixture,

adjusting the volume of said clarified green liquor being added to said slaker in response to changes in the concentration of sodium carbonate in said reaction mixture.

17. The process of claim 16 in which

said step of determining the concentration of sodium carbonate comprises

taking a sample from said reaction mixture, and

determining the concentration of sodium carbonate in said sample.

18. The process of claim 17 further comprising

removing the suspended solids from said sample prior to making said determinations of sodium carbonate concentration.

19 A process of claim 16 further comprising

transporting said reaction mixture through a plurality of serially connected causticizing vessels to allow said reaction to continue.

20. The process of claim 19 in which

said step of determining the concentration of sodium carbonate comprises

taking a sample from said reaction mixture, and

determining the concentration of sodium carbonate in said sample.

21. The process of claim 20 further comprising

removing the suspended solids from said sample prior to making said determination of sodium carbonate concentration.

22. Apparatus comprising

a pulp mill green liquor clarifier,

a slaker,

first means for transporting clarified green liquor from said green liquor clarifier to said slaker,

second means for adding liquid to said first means,

the length of said first means between said second means and said slaker allowing said green liquor and said liquid to mix and form a controlled green liquor,

third means between said second means and said slaker for determining the sodium carbonate concentration in said controlled green liquor in said first means,

fourth means responsive to said third means for adjusting flow of liquid in said second means,

fifth means for adding lime to said slaker,

sixth means for transporting a reaction mixture of green liquor, lime and reaction products from said slaker,

seventh means for determining the sodium carbonate concentration in said reaction mixture,

eighth means responsive to said seventh means for adjusting flow in said first means.

23. The apparatus of claim 22 in which

each of said third means and said seventh means comprises

means for sampling the appropriate liquor, and

an additional means for determining the sodium carbonate concentration in said sample.

24. The apparatus of claim 23 further comprising

each of said sample taking means comprises a means for removing suspended solids from said sample.

25. The apparatus of claim 22 further comprising

a plurality of serially connected causticizing vessels for allowing said reaction between green liquor and said lime to continue,

said sixth means transporting said reaction mixture from said slaker through said causticizing vessels.

26. The apparatus of claim 25 in which

each of said means for determining said sodium carbonate content comprises

means for sampling the appropriate liquor, and

means for determining the sodium carbonate concentration of said sample.

27. The apparatus of claim 26 further comprising

said sampling means has means for removing suspended solids from said sample.

28. Apparatus comprising

a slaker for reacting clarified green liquor with lime,

first means for transporting said clarified green liquor to said slaker,

second means for adding said lime to said slaker,

third means for transporting a reaction mixture of green liquor, lime and reaction products from said slaker,

fourth means for determining the sodium carbonate concentration in said reaction mixture,

fifth means responsive to said fourth means for adjusting the flow of green liquor in said first means.

29. The apparatus of claim 28 in which

said means for determining said sodium carbonate content comprises

means for sampling said reaction mixture, and

means for determining the sodium carbonate concentration of said sample.

30. The apparatus of claim 29 further comprising

means for removing suspended solids from said sample.

31. The apparatus of claim 30 further comprising

a plurality of serially connected causticizing vessels for allowing said reaction between said green liquor and said lime to continue,

said third means transporting said reaction mixture from said slaker through said causticizing vessels.

32. The apparatus of claim 31 in which

said means for determining said sodium carbonate content comprises

means for sampling said reaction mixture, and

means for determining the sodium carbonate concentration of said sample.

33. The apparatus of claim 32 further comprising

said sampling means has means for removing suspended solids from said sample.

34. Apparatus comprising

first means for clarifying pulp mill green liquor,

second means for reacting said clarified green liquor with lime,

third means for transporting said clarified green liquor from said first means to said second means,

fourth means for adding liquid to said third means,

the length of said third means between said fourth and said second means allowing said green liquor and said liquid to mix and form a controlled green liquor,

fifth means for determining the sodium carbonate concentration in said controlled green liquor in said third means at a point between said fourth means and said second means,

sixth means responsive to said fifth means for adjusting the flow of liquid in said fourth means,

seventh means for adding lime to said slaker,

eighth means for transporting a reaction mixture of green liquor, lime and reaction products from said slaker,

ninth means for determining the sodium carbonate concentration in said reaction mixture,

tenth means responsive to said ninth means for adjusting flow in said first means.

35. The apparatus of claim 34 in which

each of said fifth and ninth means comprises

means for sampling the appropriate liquor, and

an additional means for determining the sodium carbonate concentration in said sample.

36. Apparatus comprising

a recovery furnace for burning pulp mill digestion waste liquors to form inorganic smelt,

a smelt dissolving tank for forming from said smelt, particulate matter and a green liquor comprising sodium carbonate and sodium sulfide,

first means for transporting said smelt from said recovery furnace to said smelt dissolving tank,

a green liquor clarification tank,

second means for transporting said green liquor from said smelt dissolving tank to said green liquor clarification tank,

a slaker for reacting said clarified green liquor with lime to form a reaction mixture of green liquor, lime and reaction products,

third means for transporting said clarified green liquor from said green liquor clarification tank to said slaker,

fourth means for adding said lime to said slaker,

causticizing vessels for allowing said reaction between said green liquor and said lime to continue,

fifth means for transporting said reaction mixture from said slaker through said causticizing vessels,

sixth means for separating said reaction mixture into a clarified white liquor and a calcium carbonate mud,

seventh means for transporting said reaction mixture from said causticizing vessels to said separating means,

eighth means for transporting said clarified white liquor to a digester,

ninth means for washing chemical from said calcium carbonate mud to form a weak wash effluent,

tenth means for transporting said calcium carbonate mud from said separating means to said ninth means,

eleventh means for transporting said weak wash effluent from said ninth means to said smelt dissolving tank,

twelth means for transporting a portion of said weak wash effluent to said third means,

thirteenth means for determining the sodium carbonate concentration in a mixture of said clarified green liquor and said weak wash at a point prior to said slaker,

fourteenth means responsive to said thirteenth means for adjusting the flow of weak wash in said twelfth means,

fifteenth means for determining the sodium carbonate concentration in said reaction mixture,

sixteenth means responsive to said fifteenth means for adjusting flow in said third means.

37. The apparatus of claim 36 in which

each of said means for determining said sodium carbonate content comprises

means for sampling the appropriate liquor, and

means for determining the sodium carbonate concentration of said sample.

38. Apparatus comprising

a first means for burning pulp mill digestion waste liquors to form an inorganic smelt,

second means for dissolving said smelt to form particulate matter and a green liquor comprising sodium carbonate and sodium sulfide,

third means for transporting said smelt from said first means to said second means,

fourth means for clarifying said green liquor,

fifth means for transporting said green liquor from said second means to said fourth means,

sixth means for reacting said clarified green liquor with lime to form a reaction mixture of green liquor, lime and reaction products,

seventh means for transporting said clarified green liquor from said fourth means to said sixth means,

eighth means for adding said lime to said sixth means,

ninth means for allowing said reaction between said green liquor and said lime to continue,

tenth means for transporting said reaction mixture from said sixth means to said ninth means,

eleventh means for separating said reaction mixture into a clarified white liquor and a calcium carbonate mud,

twelfth means for transporting said reaction mixture from said ninth means to said eleventh means,

thirteenth means for transporting said clarified white liquor to a pulp mill digester,

fourteenth means for washing chemicals froms said calcium carbonate mud to form a weak wash effluent,

fifteenth means for transporting said calcium carbonate mud from said eleventh means to said fourteenth means,

sixteenth means for transporting said weak wash effluent from said fourteenth means to said second means,

seventeenth means for transporting a portion of said weak wash effluent from said seventeenth means to said fifth means,

eighteenth means for determining the concentration of sodium carbonate in the mixture of said clarified green liquor and said weak wash in said fifth means,

nineteenth means responsive to said eighteenth means for adjusting the flow through said seventeenth means,

twentieth means for determining the sodium carbonate concentration in said reaction mixture,

twenty-first means responsive to said twentieth means for adjusting flow in said seventh means.

39. The apparatus of claim 38 in which

each of said means for determining said sodium carbonate content comprises

means for sampling said appropriate liquor, and

means for determining the sodium carbonate concentration of said sample.

1/9

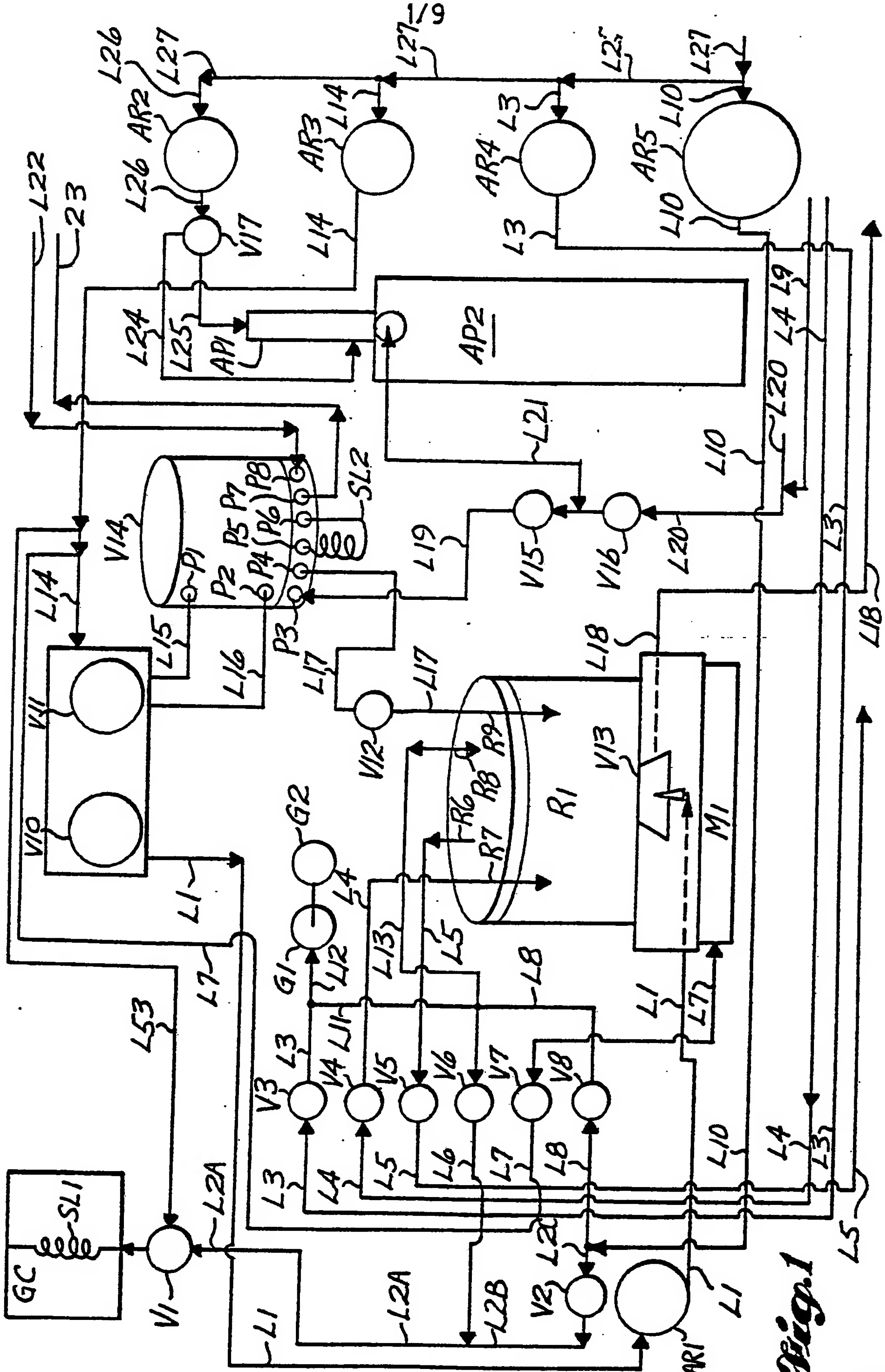
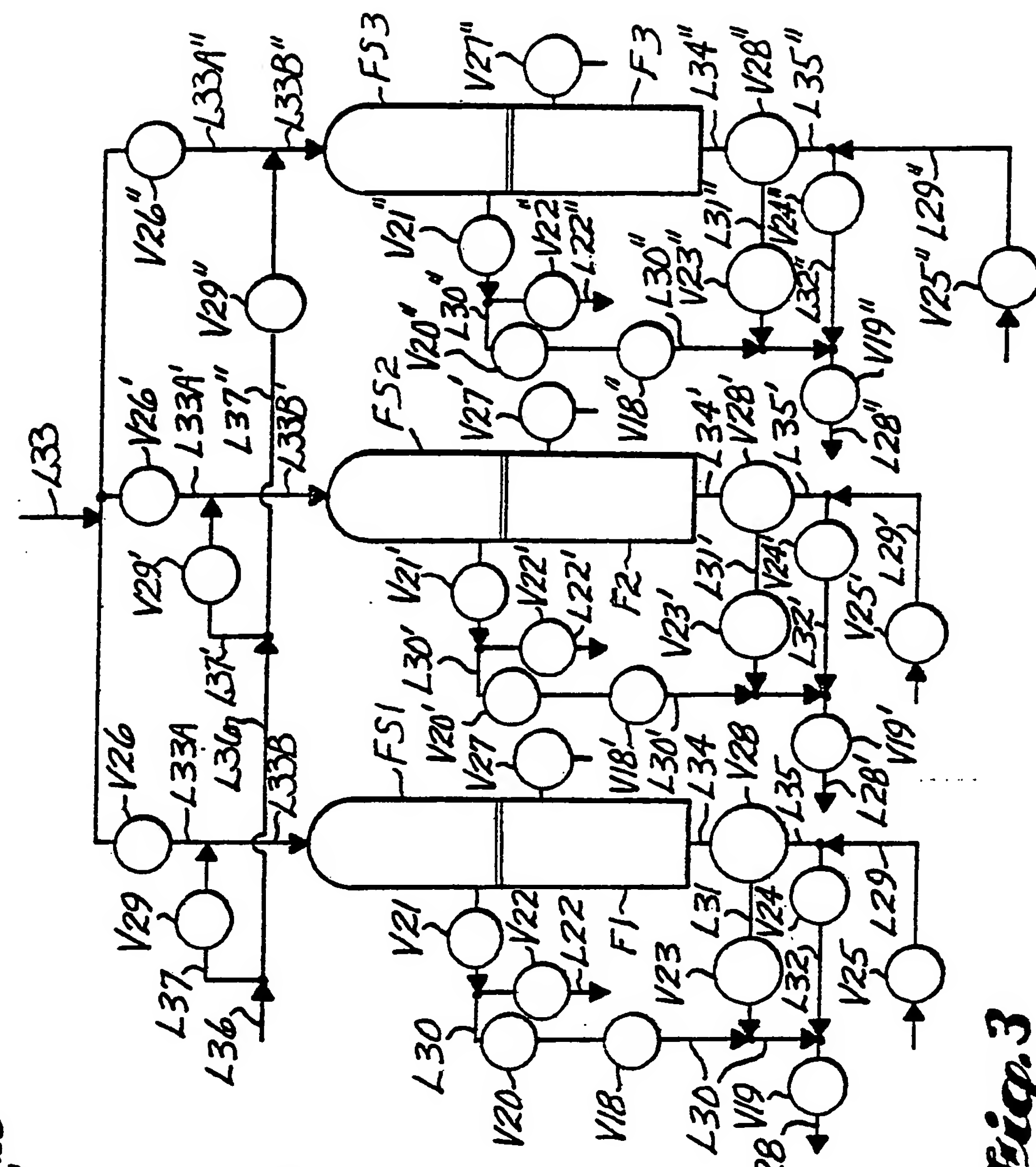
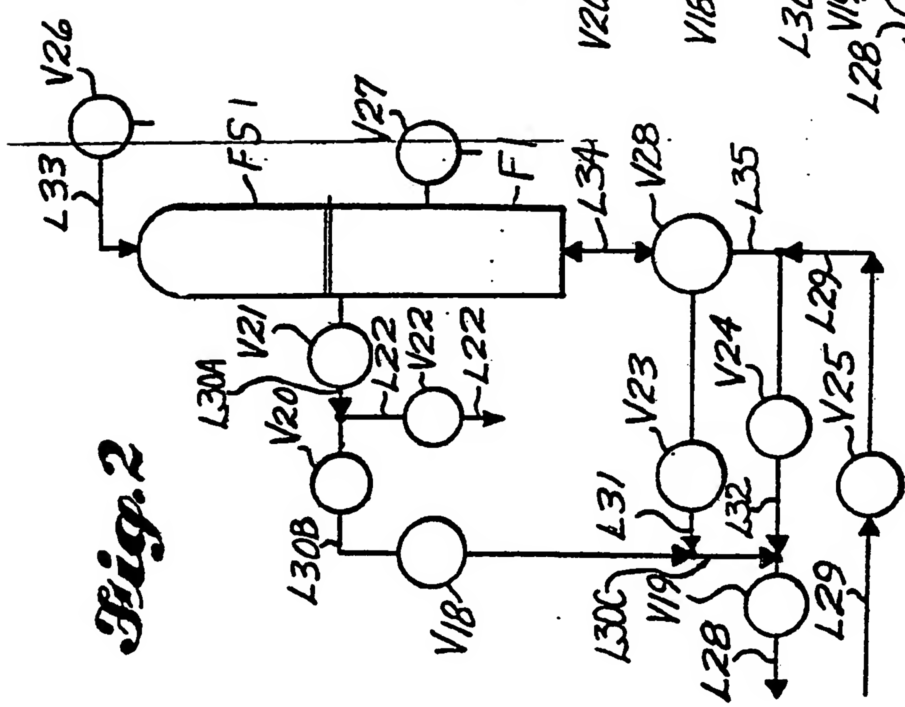

L26
L27
AR2
AR3
AR4
AR5
L14
L3
L10
L25
L22
23
V17
L24
AP1
AP2
L21
L20
L9
L4
SL2
P1
P2
P3
P4
P5
P6
P7
P8
V14
V15
V16
L19
L15
L16
L17
V11
V10
V12
L18
R1
R6
R7
R8
R9
V13
M1
G1
G2
L1
L7
L53
L12
L13
L5
L8
L11
V1
V2
V3
V4
V5
V6
V7
V8
L6
L2A
L2B
L2C
GC
SL1
AR1

Fig.1



L33
L33A''
L33B''
FS3
F3
V26''
V27''
V28''
L34''
L35''
V29''
V21''
V22''
L22''
V20''
L30''
V23''
L31''
V24''
L32''
V25''
L29''
V18''
V19''
L28''
V26'
L33A'
L37''
L33B'
FS2
F2
V27'
V28'
L34'
L35'
V29'
V21'
V22'
L22'
V20'
L30'
V23'
L31'
V24'
L32'
V25'
L29'
V18'
V19'
L28'
L37'
V26
L33A
L36
L33B
FS1
F1
V27
V28
L34
L35
V29
L37
V21
V22
L22
V20
L30
V23
L31
V24
L32
V25
L29
V18
V19
L28

Fig. 3



V26
L33
FS1
V27
F1
L34
V28
L35
V21
L30A
V20
L22
V22
V23
V24
L29
V25
L31
L32
L30B
V18
L30C
V19
L28

Fig. 2

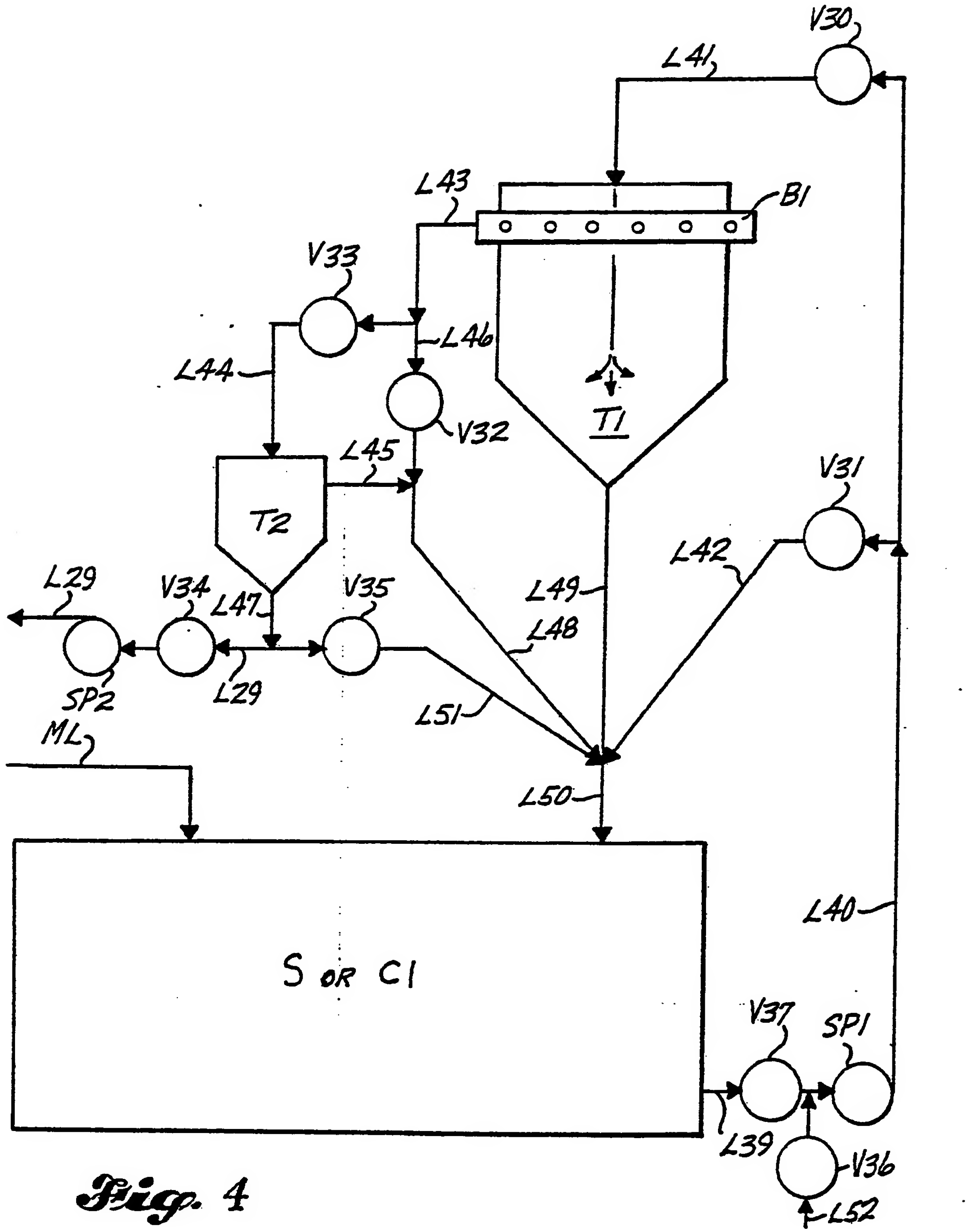

V30
L41
L43
B1
V33
L46
L44
V32
T1
L45
T2
V31
L42
L29
V34
L47
V35
L49
L48
SP2
L29
L51
ML
L50
S OR C1
L40
V37
SP1
L39
V36
L52

Fig. 4

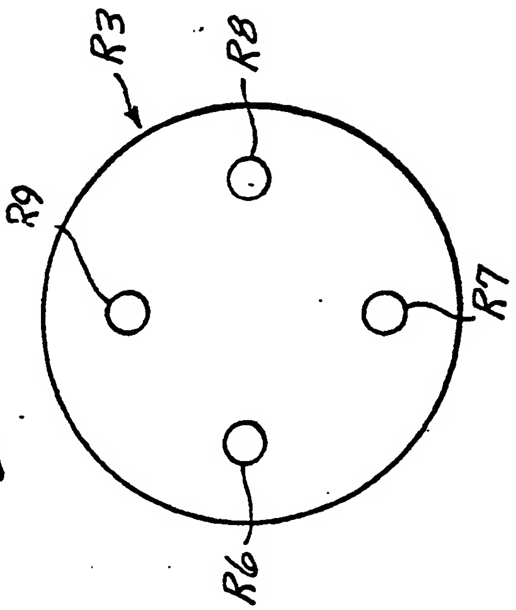

R3
R8
R9
R7
R6

Fig.6

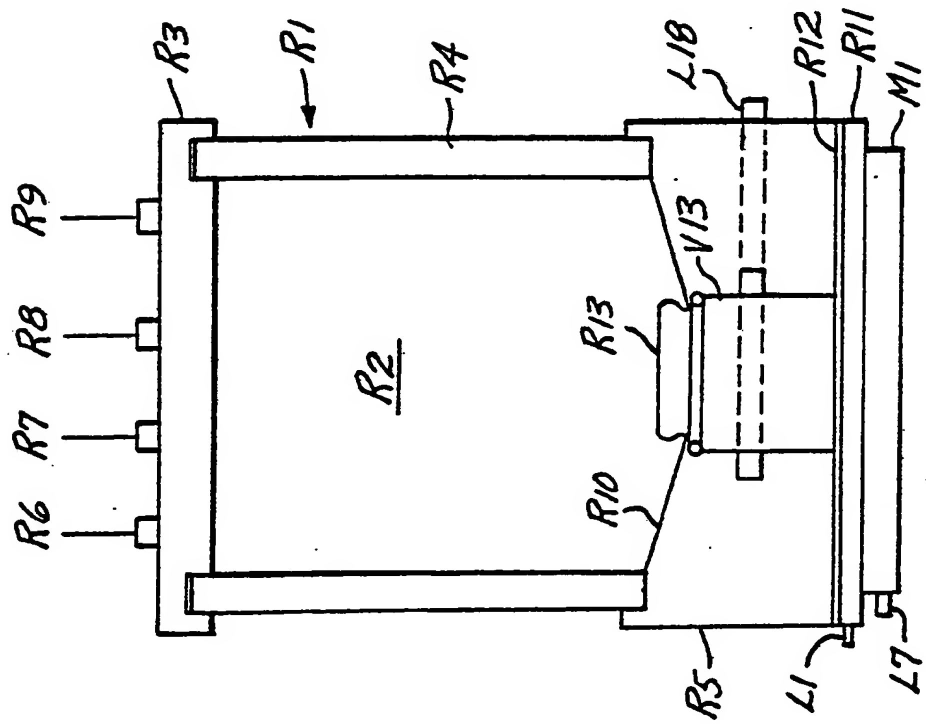

R3
R1
R4
L18
R12
R11
M1
R9
V13
R8
R13
R2
R7
R10
R6
R5
L1
L7

Fig.5

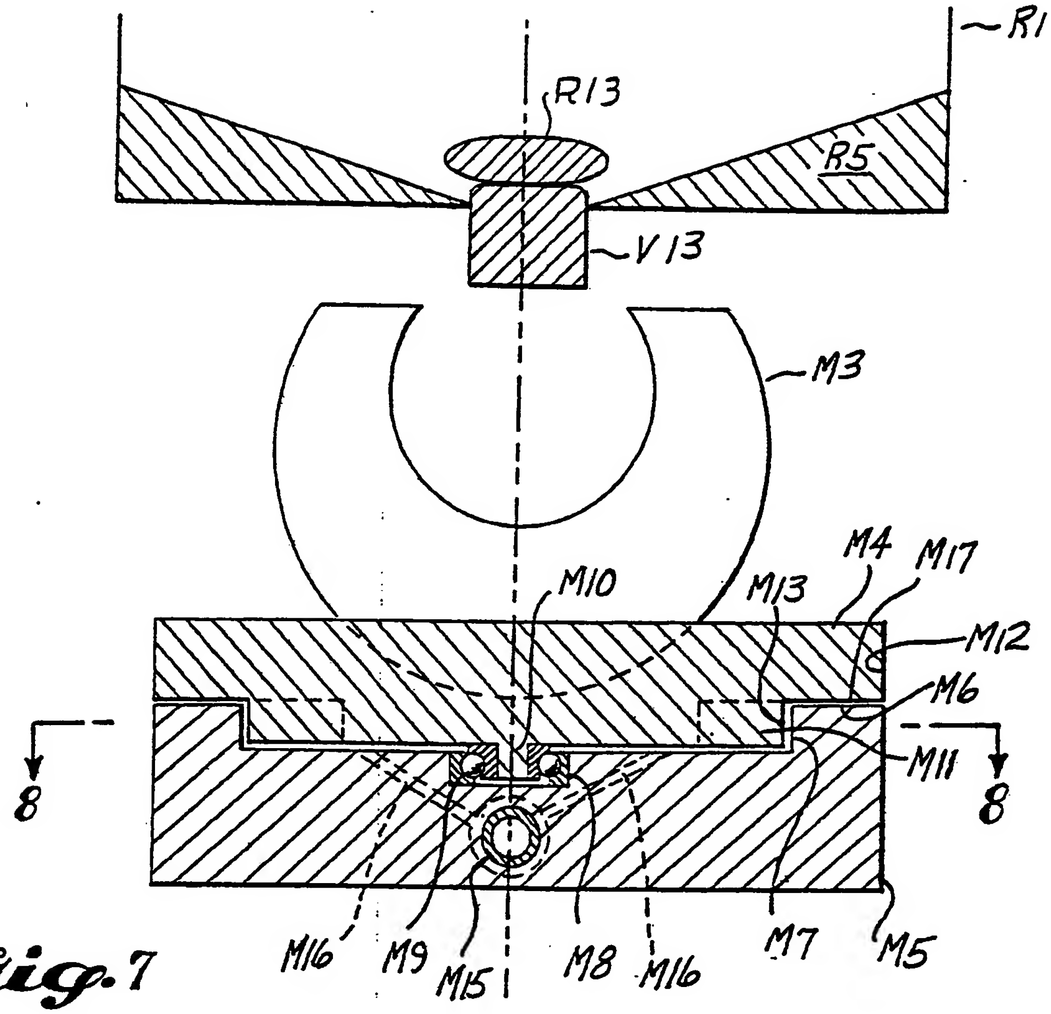

R1
R13
R5
V13
M3
M4
M17
M10
M13
M12
M6
M11
8
8
M16
M9
M15
M8
M16
M7
M5

Fig. 7

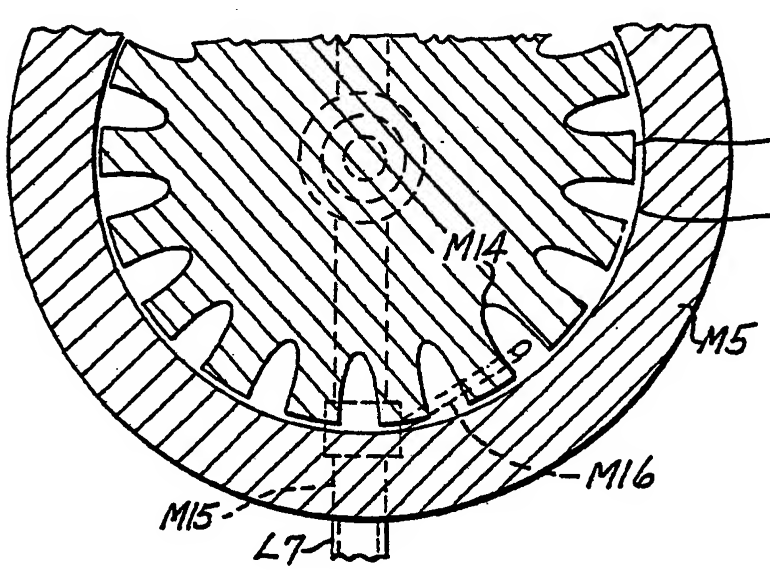

M13
M7
M14
M5
M16
M15
L7

Fig. 8

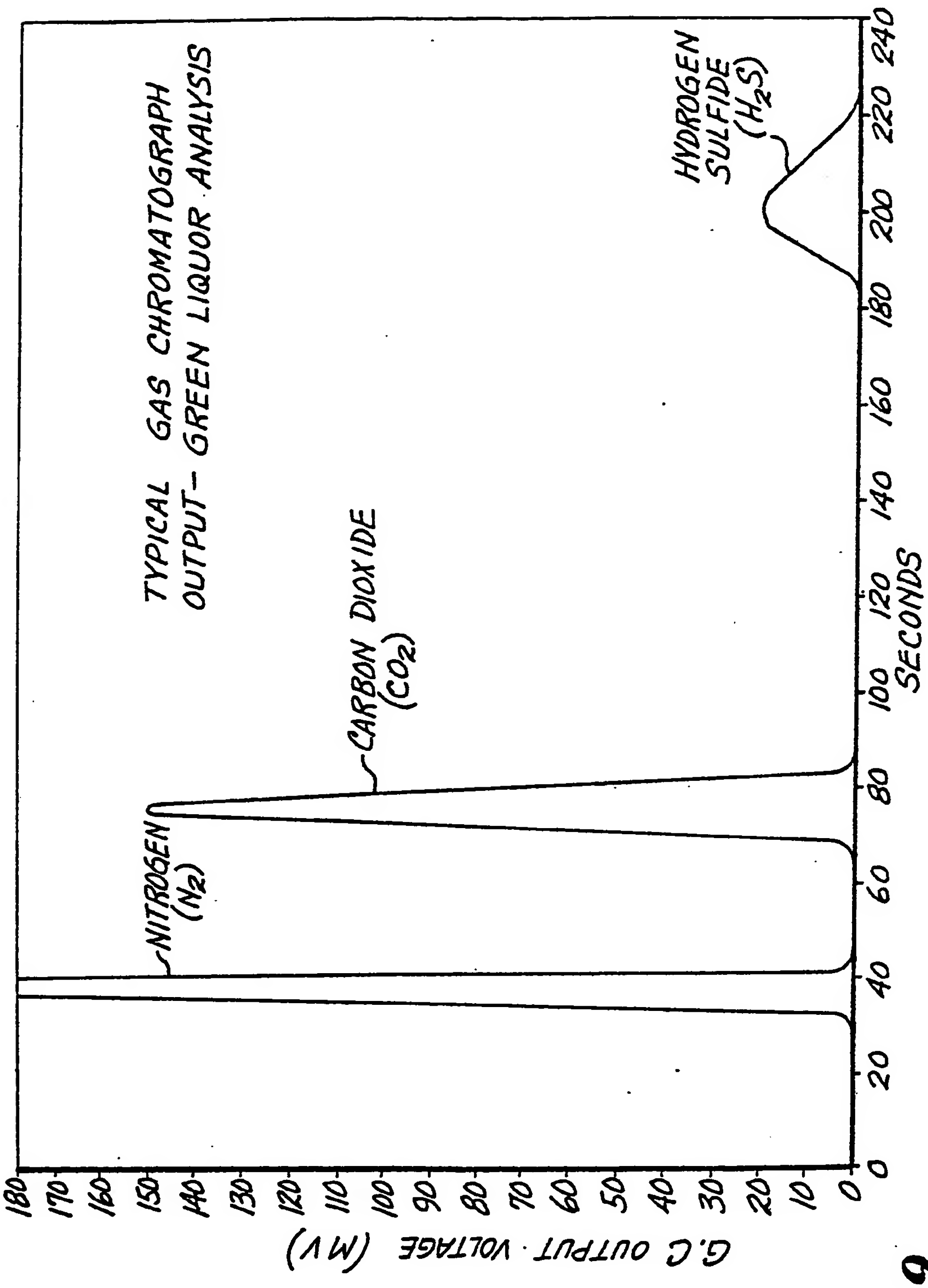
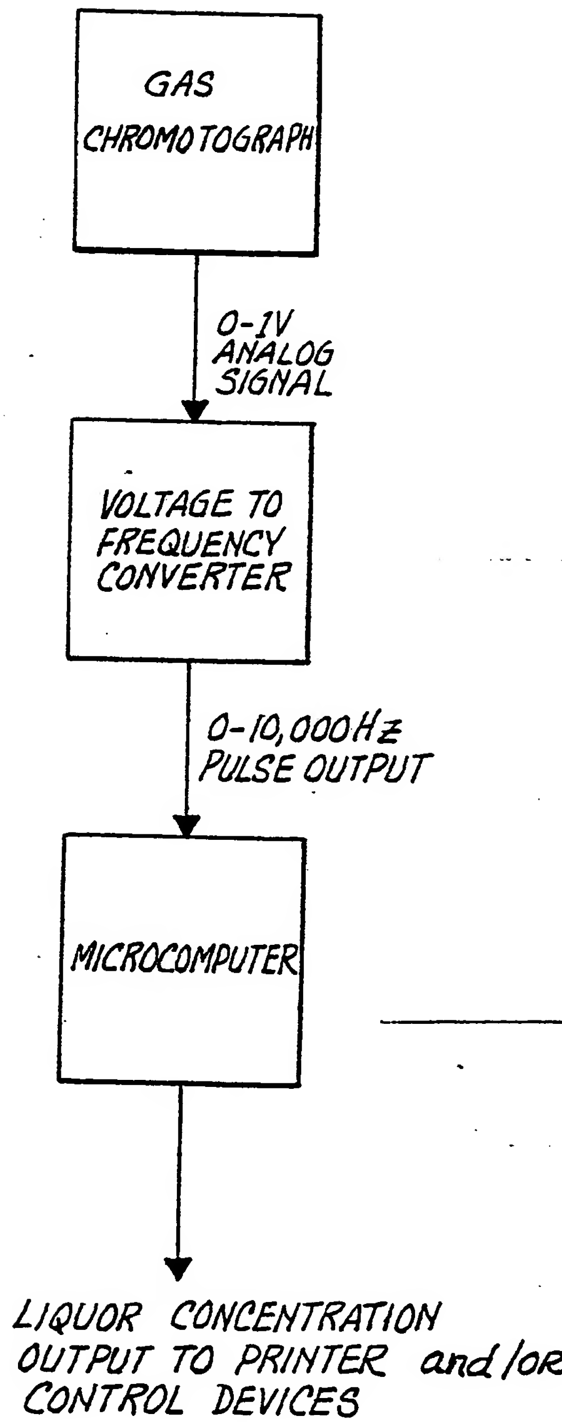

TYPICAL GAS CHROMATOGRAPH
OUTPUT- GREEN LIQUOR ANALYSIS
NITROGEN
(N2)
CARBON DIOXIDE
(CO2)
HYDROGEN
SULFIDE
(H2S)
SECONDS
G.C OUTPUT · VOLTAGE (MV)
0
20
40
60
80
100
120
140
160
180
200
220
240
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

Fig. 9

Fig. 10


GAS CHROMOTOGRAPH
0-1V ANALOG SIGNAL
VOLTAGE TO FREQUENCY CONVERTER
0-10,000Hz PULSE OUTPUT
MICROCOMPUTER
LIQUOR CONCENTRATION OUTPUT TO PRINTER and/or CONTROL DEVICES

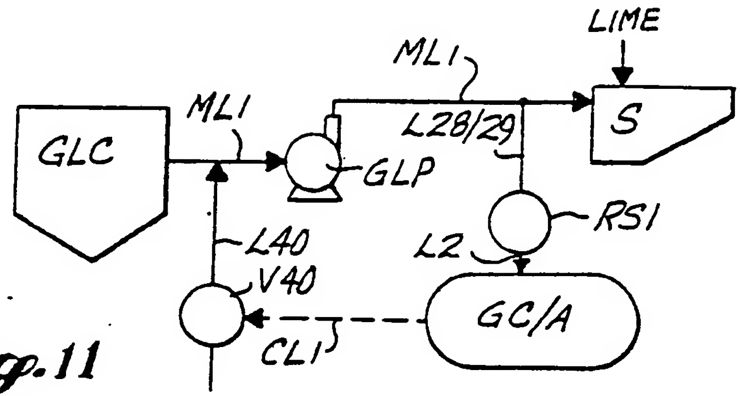


Fig. 11

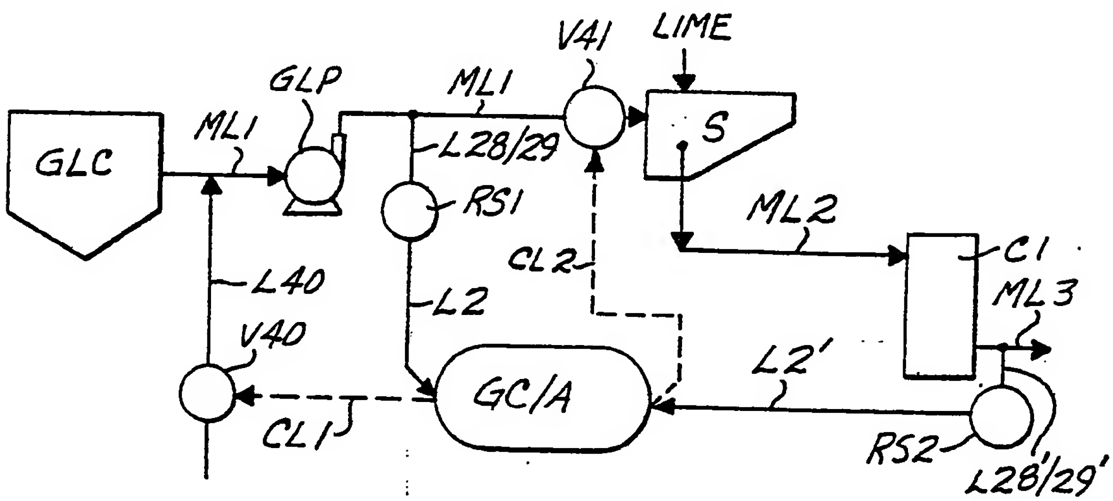


Fig. 12

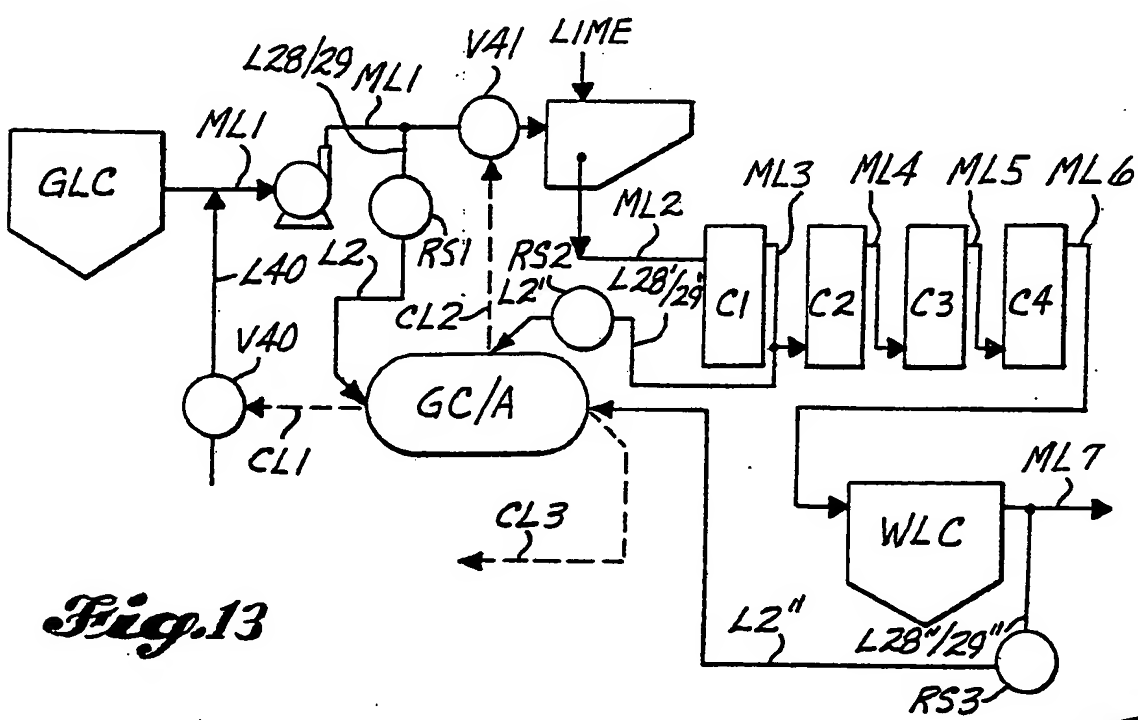


Fig. 13

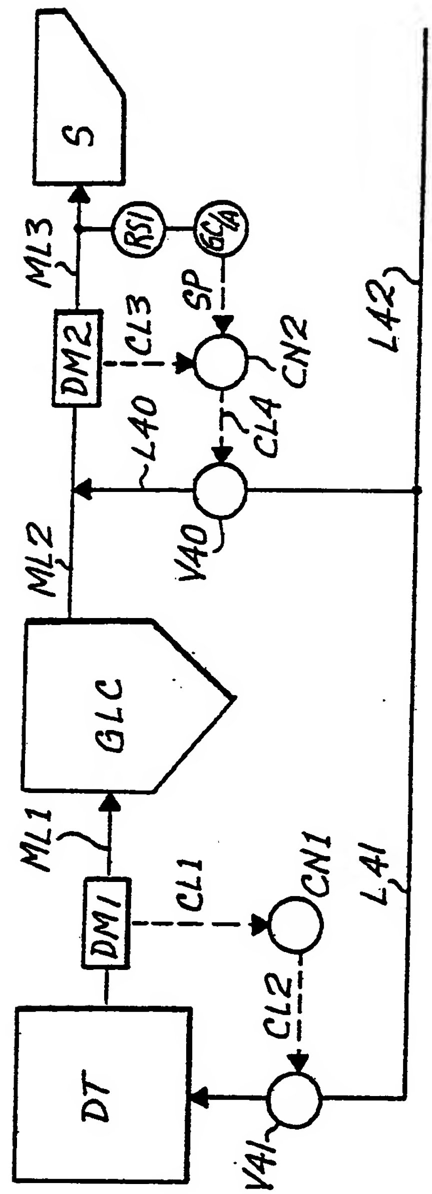

S
ML3
RSI
GC/A
SP
DM2
CL3
CN2
L42
L40
CL4
ML2
V40
GLC
ML1
DM1
CL1
CN1
L41
CL2
DT
V41

Fig.14

INTERNATIONAL SEARCH REPORT

International Application No PCT/US84/00739

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to I[illegible] [illegible]nal Patent Classification (IPC) or to both National Classification and IPC

INT. CL.[3] D21C 11/04, D21C 11/12

U.S. CL. 162/30.11, 49, 62 422/62, 80, 185

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	162/30.1,30.11,49,62,238,263,DIG 10 422/62,68,80,185 423/207,DIG 3

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	N, PROCESS ISA SYMPOSIUM (MEETING PAPER), ISSUED OCTOBER 1975, JACOBI ET AL, MODELING AND CONTROL KRAFT PRODUCTION SYSTEMS, SEE PAGES 187-202.	1-39
A	N, BUMAZH. PROM. 24, NO. 3:6-11, ISSUED MAY/JUNE 1949, DENISOV, PRINCIPLES OF THE TECHNOLOGICAL PROCESS OF KRAFT LIQUOR CAUSTICIZATION.	1-39
A	N, PULP AND PAPER MANUFACTURE, SECOND EDITION, VOL I, ISSUED 1969, MACDONALD, ED., SEE PAGES 534-536.	1-39
A	US,A, 4,311,666, PUBLISHED JANUARY 19, 1982, HULTMAN ET AL.	1-39
A	US,A, 4,192,708, PUBLISHED MARCH 01, 1980, BERGSTROM ET AL.	6,9,12,15,18,21 24,30,33

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
26 JULY 1984	07 AUG 1984
International Searching Authority [1]	Signature of Authorized Officer [20]
ISA/US	Steven Alvo STEVEN ALVO

Form PCT/ISA/210 (second sheet) (October 1981)

See notes on accompanying sheet